REACTIVE PLASMA ATOMIZATION OF ALUMINUM NITRIDE POWDER

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Abstract

Experiments were performed to synthesize AlN powders by reacting Al with N using a conventional DC arc plasma as a heat source. Attempts to form AlN powders by feeding Al powder into an argon/nitrogen plasma open to the atmosphere produced mainly aluminum oxide. Subsequent experiments were run inside a chamber which was backfilled with nitrogen. The nitrogen environment suppressed the formation of aluminum oxide, but little AlN was formed by using Al powder as the feedstock material. A furnace and crucible assembly was designed to feed molten Al directly into a DeLaval nozzle attached to the face of the DC arc plasma gun. The submicron powders formed using this arrangement show a significant increase in the level of AlN formation. The presence of AlN was verified by chemical analysis and X-ray diffraction. Results were dependent upon chamber pressure, plasma velocity and molten liquid feed rate. The experimental parameters, equipment design and results will be reported in detail. The effects of atomization, vaporization and condensation on the reaction product will be discussed.

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Introduction

There are many methods to produce AlN powder [1-3]. Commercial production of AlN uses either the carbothermal reduction of Al_2O_3 or the nitridation of aluminum powder by a fluidized bed [1]. The direct nitridation of aluminum powder occurs between 1300°C and 1600°C with a residence time of 2-3 seconds [2]. The primary interest in AlN is the unusual property combination of high thermal conductivity (200W/m-K) with a high electrical resistivity (>10¹⁴ Ω cm) [3]. The AlN material has distinct advantages for thermal management applications in multilayer chips. Other potential applications are for high conductivity refractory materials for investment casting shell systems, composite particulate reinforcement or advanced spark plug materials. [3,4]

The use of a reactive plasma to produce ceramic compounds has been described in a review by Young and Pfender [4]. Nitrogen plasma has been used with a mixture of reactive gases such as CH_4 , NH_4 , BCl_3 , $TiCl_4$, and $AlCl_3$ in plasma reactors to produce nanocrystalline powders of TiN, TiC, TiB_2 and AlN with hazardous by-products of ammonia, chlorine, hydrogen chloride and hydrogen gas [5-11]. The reaction between aluminum powder and nitrogen plasma has been reported to produce fine AlN powder [3,5]. Other investigators fed aluminum powder into an R.F. nitrogen plasma and found the addition of ammonia gas was necessary to produce high yields of AlN powder [7]. Although the reactions between gases and solids with plasma have been extensively studied, very little work has been reported on the introduction of a molten metal into a plasma torch.

German has described a "Horizontal Atomization" process used for the production of tin originating in the 1920's, shown in Figure 1 [12]. The technique consists of introducing the molten tin into a high velocity gas stream that is flowing across the orifice of a vertical melt feed tube. The atomization occurs as the gas creates a low pressure zone above the feed tube. The molten metal is siphoned into the gas flow, which shears the liquid into droplets and accelerates them into the chamber. The efficiency of production of fine particles was reported by Lenel to be a strong function of this venturi type of nozzle design and process parameters, but no references were provided [13]. Swank, Fincke and Mason [14] at Idaho National Engineering Laboratory (INEL) recently investigated the atomization mechanisms in such venturi atomization, also known as DeLaval atomization. This work used an apparatus similar to that shown in Figure 1, but a heated gas was used to control the deposition behavior during spray forming. The nozzle was designed as a convergent-divergent geometry to maximize the suction and improve atomization efficiency. Berry et al. [15] developed a model to predict the gas flow, atomization phenomena and droplet solidification in the INEL DeLaval nozzle. However, the influence of nozzle geometry on atomization efficiency of these nozzles was not well described.

The knowledge of the gas flow and of the thermal characteristics of the plasma are important for understanding the behavior of a molten metal introduced into the plasma plume. Fortunately, the temperature and velocity characteristics of an argon/helium plasma from Miller Thermal SG-100 plasma gun with a subsonic anode/cathode have been measured by Fincke and Swank [16]. Also, the inflight temperature of alumina particles was measured as an indication of heat transfer. Since the present investigation used a similar plasma gun and operating parameters, the thermal behavior of the molten aluminum droplets will be inferred using the Fincke and Swank results [16]. Finally, the thermodynamics of phase equilibria during condensation of plasma reactions has been studied by Chang and Pfender [21]. This investigation will use a similar methodology to describe the mechanism of product formation.





Experimental Procedure

A few experiments were conducted with conventional feeding of aluminum powder into a plasma gun to establish a baseline nitrogen and oxygen levels for air plasma spray (APS) and chamber plasma spray (CPS). Reactive Plasma Atomization (RPA) was conducted in the controlled environment of the chamber. However, instead of introducing the aluminum into the plasma by a conventional powder feeder, superheated molten aluminum was fed into the DC arc plasma torch to atomize the liquid metal into droplets and to react the liquid droplets with an argon/nitrogen plasma to produce a fine AlN powder.

Reactive Spraying of Aluminum Powder

Spherical aluminum powder from Alcan-TOYO was fed into a plasma spray gun in the initial attempts to produce aluminum nitride powders. The aluminum powder diameter was an average of 25 microns and had an initial oxygen content of 0.2 wt.% oxygen. The APS experiments were conducted in air at atmospheric pressure in a simple collection apparatus constructed from 8 inch diameter metal tube. The gun was fastened to the tube to minimize the reaction with the air. The tube was purged with the argon for 2 minutes prior to spraying to reduce oxygen in the environment. The aluminum powder was fed at 2.7 g/min, the argon flow was 40 l/min, the nitrogen flow was 25 l/min, the gun voltage was 60 volts and the gun amperage was 600 amps, 800 amps and 1000 amps. The CPS experiments were conducted in the spray chamber with an atmospheric pressure of nitrogen to prevent the oxidation of aluminum, and promote the formation of aluminum nitride. The nitrogen and oxygen were measured by an inert gas fusion technique. X-ray diffraction was conducted on the powder product to identify peaks for aluminum, aluminum oxide or aluminum nitride.



Figure 2 - Schematic of Reactive Plasma Atomization Equipment_

Reactive Plasma Atomization

A melt crucible and extension nozzle were designed for attachment to the face of the Miller Thermal SG-100 plasma gun, shown in Figure 2. The graphite nozzle with an 18° divergent angle was attached to the plasma gun to control the expansion of the plasma. A graphite crucible with a small feed hole was attached to feed molten metal at 90° into the graphite nozzle at the point of divergence 25 mm from the face of the plasma gun, shown in Figure 3. The liquid feeding for RPA depended primarily of the hydrostatic head pressure instead of a suction pressure as described for the horizontal atomizer and INEL DeLaval atomizer. The entire apparatus was enclosed in a vacuum chamber (<10⁻² torr) in order to prevent oxidation and promote nitridation of the molten aluminum droplets. The graphite crucible was charged with 60 to 80 grams of 99.99% aluminum rod. A resistively heated kanthal furnace surrounded the graphite crucible such that the aluminum melt stock was melted (660°C) and superheated to 1000°C. The temperature of the furnace and the molten bath were monitored with type-K thermocouples. When the melt temperature reached the desired level, the chamber was backfilled to the desired operating pressure (200 torr or 720 torr).



Figure 3 - Crucible and Nozzle Configuration for Reactive Plasma Atomization

The operating parameters for the SG-100 gun were an argon flow of 40 l/min, a nitrogen flow of 25 l/min, a gun voltage of 60 volts and a gun amperage was 600 amps. A few minutes after the plasma gun was started, the thermal energy from the plasma heated the graphite nozzle sufficiently to allow the aluminum to drain through the feed hole in the bottom of the crucible. The superheated molten aluminum was gravity fed into the graphite nozzle and atomized into fine droplets by the plasma plume. The atomized droplets were accelerated and were heated to a liquid/vapor by the plasma, while reacting with the nitrogen in the plasma plume.

Four experiments were devised using a partial factorial orthogonal array to examine the effects of 3 major parameters on the degree of reaction occurring during the spraying. The major variables were plasma velocity, chamber pressure and metal feed rate. The plasma velocity was varied by using a "Mach I" or subsonic anode/cathode combination with the Miller SG-100 plasma gun. The metal feed rate was estimated by a water flow test through the desired hole size, and a density correction of 2.5 g/cm³ was used for molten aluminum. The lower metal flow rate was estimated to be 16 g/min, and the high metal flow rate was estimated to be 34 g/min, as shown in Table I. These flow rates were higher than the aluminum powder feed rates (2.7 g/min), but the lowest flow rate was determined by the smallest hole capable of being drilled into the bottom of the graphite crucible. The metal flow rates were only estimates due to the differences in the density, viscosity and surface energy of water and aluminum.

Table I - Estimated Molten Aluminum Flow

Hole Size	Water Flow Rate	Estimated Aluminum Flow Rate [g/min]
0.38	6.5	16.2
0.51	13.7	34.2

Experiment	Anode/Cathode	Chamber Pressure	Metal Flow Rate	
133A	Subsonic	200 torr	low	
133B	Subsonic	720 torr	high	
133C	Mach I	720 torr	low	
133D	Mach I	200 torr	high	

Table II- Reactive Plasma Atomization Parameters

The experimental matrix comprised 50% of the possible combinations of the three variables at 2 levels. Table II represents the combinations which were selected to run. Other parameters which may have an impact were fixed: melt temperature, gas mixture, gun amperage, gun voltage, gas flow, collector temperature, graphite nozzle design. Since the bottom of the crucible experienced different thermal conditions depending on the processing parameters, the time to initiate the pour varied with each experiment from approximately 1 minute to 8 minutes. The collector temperature was also a function of the time to initiate a pour, since the plasma plume was in contact with the collector prior to the initiation of metal flow. The lower chamber pressures (200 torr) extend the length of plasma plume, which transferred heat to the collector more efficiently than at ambient pressure (720 torr). This phenomena was not anticipated, and therefore the collector temperature for each run was unknown. However, the collector temperature was believed to affect the nucleation temperature of the reaction product, and therefore influence the product composition.

Powder was collected from the collection cyclone and the chamber walls. The powder in the collection cylinder was removed by sweeping sides with a paint brush. The chamber walls were vacuumed for each run with a Nilfisk HEPA filter vacuum. The vacuum bags were changed each time, so as not to cross-contaminate powder from the different runs. The powders were examined with a field emission source SEM for size and morphology. The crystal structure of the reacted powder samples were determined by an x-ray diffractometer scanning from 20° to 100° at 0.05° intervals for 3 seconds. The x-ray diffraction peaks were compared with standard peaks for Al, AlN and various forms of aluminum oxide.

Experimental Results

Reactive Spraying of Aluminum Powder

A high amount of "sooting" was observed during the plasma spraying in air (35-A,C), which indicated vaporization of the aluminum powder and a subsequent reaction with entrained air. Table III shows the chemistry data of the APS and CPS powders. The APS powder oxygen content of 38.7 wt.% indicated the aluminum was approximately 75% converted into aluminum oxide due to reaction with the entrained air. The level of AlN was approximately 2% with the remaining product presumed to be aluminum. The presence of aluminum was indicated by the x-ray diffraction, but the aluminum oxide and aluminum nitride were not observed. Since the plasma reacted powder had particles on the order of 10 nm to 100 nm, the peaks other than aluminum were broad and diffuse, typical of nanoscale powders.

	Composition (w/o)			Spraying Atmosphere	
Material	Al	N	0	Air	N ₂
Starting Powder	99.8	0.001	.2	· · · · · · · · · · · · · · · · · · ·	
AlN*	65.8	34.2			
Al ₂ O ₃ *	52.9		47.1		
35-A	61.1	0.7	38.2	X	
35-C	67.5	0.8	31.7	X	
37-A	97.3	1.1	1.6		X
37-B	98.1	1.0	0.9		X
37-C	95.4	3.9	0.7		Х

Table III - Processing Parameters for Air Plasma Sprayed Aluminum with Nitrogen

* Composition of pure compound

The experiments conducted in the chamber backfilled with nitrogen (37-A,B,C) were successful in reducing the oxygen to 1%, and increasing the nitrogen content to 3.9 wt.%. Since a pure AlN would be 34.2 wt.%, the nitrogen level of 3.9% represented approximately a 10% conversion to AlN. The remainder of the product was unreacted aluminum.

Reactive Plasma Atomization

The chemical analysis shown in Figure 4 and x-ray diffraction shown in Figure 5 indicate the results of processing conditions for runs 133A, 133B, 133C and 133D. Figure 4 shows the relationship between the collected powder and the nitrogen, oxygen and carbon contents. The highest level of nitrogen (22.6%) was observed in powder 133A with the subsonic plasma, at a chamber pressure of 200 torr and the lower metal flow rate of approximately 15 g/min. The lowest level nitrogen (0.69%) was achieved in powder 133D with a Mach I plasma, at a chamber pressure of 200 torr and a high metal flow rate. The other runs 133B and 133C showed moderate nitrogen levels (8.5%). In the best case, 133A, the molten aluminum was converted 67% to aluminum nitride. The powder removed from the bottom of the collector after run 133A was flowable and high density. The other powders were very difficult to handle due to a chain like structure of crystallites. The SEM examination of this powder indicated agglomerates ranging from 10 µm to 100 µm of the small crystallites ranging from 50 nm to 100 nm shown in Figure 6. The agglomerates were believed to form due to the higher temperature of the collector. The nanoscale particles were a product of the vaporization of aluminum, reaction with the gaseous species, and homogeneous condensation in the plasma plume or heterogeneous condensation on the collector walls. A higher collector temperature would affect the condensation temperature, and therefore would produce a different thermodynamic phase equilibria between aluminum, aluminum nitride and nitrogen gas.



Figure 4 - Chemistry of Reactive Atomization Powder



Figure 5 - X-ray Diffraction for the Reactive Plasma Atomized Powders



Figure 6 - Agglomerated Powder produced in Collector from Run 133A

Since no protective measures were taken to isolate the powder from air or moisture, oxygen may have contaminated the product after the processing. The oxygen content was believed to be a product of a thin adsorbed surface layer. High aluminum containing fine powders have been demonstrated to absorb moisture and oxygen on the surface. A simple computer model was constructed which predicts the bulk oxygen level for a 10Å thick film of aluminum oxide on aluminum powders ranging from 10 nm to 100 nm in diameter. Figure 6 shows a theoretical curve compared to the shaded region representing the range of oxygen contents observed in RPA powders.





Discussion

The reaction mechanisms for AIN in the RPA process had three stages, which are sequentially dependent on each other. The first stage was the atomization, which was a result of the high velocity plasma/melt interaction in the convergent-divergent nozzle. The second stage was the vaporization, which was dependent on the surface area of the atomized droplet, the remaining thermal energy in the plasma, the droplet velocity within the plasma, and the dwell time for interaction. The third stage was the temperature of the gaseous products, which determined the phase equilibria during the condensation of the final product. The plasma processing parameters had an impact on each reaction stage, which were sometimes in conflict with each other to produce the maximum reaction condition.

Atomization

In general, the gas/metal ratio and the gas velocity are the most important parameters in liquid metal atomization. A dimensionless parameter, the Weber number, provides an indication of the stability of a particular droplet size in a specific gas flow field. The expression below defines the Weber number, We, where, ρ_{GAS} is the density of the gas, V is the velocity of the gas, d_{DROP} is the diameter of the droplet, and σ_{LIQ} is the surface tension of the liquid. For example, Krzeczkowski observed when the Weber number exceeds a critical value of 13, the droplet will continue to break up until the minimum diameter droplet satisfies the criteria We_{CRIT} < 13 [17].

$We_{CRIT} = \rho_{GAS} V^2 d_{DROP} / \sigma_{LIQ}$

Therefore, a supersonic gas would be the most effective for atomizing powder. However, supersonic velocity gases can lose a large proportion of kinetic energy due to an underexpanded condition created by the exit of the nozzle [18]. The atomization mechanisms in the DeLaval spray forming nozzle were investigated at INEL used a number of diagnostic techniques [14]. A computer model for the gas flow field and atomization of droplets has been developed to assist in the design of DeLaval atomization nozzles [15]. Both the diagnostic techniques and the computational modeling would be useful in assessing the plasma interaction with molten droplets. Since the gas velocity profile and particle interaction were not measured in this investigation, we must approximate them from previous work to conduct a general assessment of the RPA atomization characteristics.

Plasma Temperature and Gas Flow

The gas velocity and temperature distributions for a Miller Thermal SG-100 with a subsonic anode/cathode combination using argon-helium gas are shown in Figure 8 [16]. The maximum temperature of the plasma was approximately 13,000K at the exit from a torch, while the maximum gas velocity was about 1500 m/s at the centerline of the exit of the plasma flow. The temperature and velocity decreased as a function of the axial distance from the exit of the gun and as a function of radial distance from the centerline. At 40 mm from the exit of the gun the plasma temperature diminished to 4000 K and the gas velocity decayed to 400 m/s. While 5 mm off centerline at the same axial distance, the plasma temperature was reduced to 3000 K, and the gas velocity was reduced to 200 m/s.



Figure 8 - Velocity profile of Miller Thermal SG-100 subsonic Ar/He plasma in air [16]

The temperature profile of alumina particles with an average diameter of 25 μ m with a feed rate of 25 g/min is shown as a function of distance in Figure 9, which also indicates the temperature increase above the alumina melting point. The thermal energy used to melt the alumina represented less than 5% of the 30 kW input or approximately 1 kW. The acceleration of the alumina particles through the plasma allows for approximately 0.25 milliseconds of residence time in the plasma [16]. The lower chamber pressure (200 torr) increases the velocity and plasma plume length. However, the effect on residence time is unclear, and the data from reference [16] may only be used comparatively with the subsonic gun conditions at high chamber pressure (720 torr). The energy transfer of 1 kW may be used as an approximation to calculate the heat transfer to molten aluminum droplets, which produced aluminum vaporization with the subsonic gun conditions at 720 torr.





Vaporization

A heat balance calculation shows that approximately 1 kW from the plasma gun operating at 36 kW was transferred to the alumina powder. If the same 1 kW were transferred to aluminum liquid at 1000°C, then 5 g/sec of aluminum would be vaporized at the boiling point of 2450°C. Since the highest metal feed rates in this investigation were approximately 0.5 g/sec, it appeared

the power requirement for complete vaporization was satisfied. The energy transfer to the molten aluminum depended on the atomized droplet size and velocity. The maximum atomization would occur with higher gas velocities, which would produce the maximum droplet surface area to enhance vaporization. Conversely, the high droplet velocities would reduce the dwell time to inhibit vaporization. Therefore, the competing phenomena of atomization and droplet acceleration must be balanced to obtain the optimum vaporization conditions.

Thermodynamic Phase Equilibria

The SOLGASMIX thermodynamic computer program [20] was used to predict the competition between aluminum oxide formation and aluminum nitride formation in a plasma environment. The consideration of the equilibrium condition and nucleation theory provided insight as to the origin of phase mixture observed in the reactive sprayed product. Chang and Pfender [21] considered the following rules using the classical approach for homogeneous nucleation to condensed phase products from gaseous species:

1. The gas-phase reaction will proceed until the supersaturating ratio exceeds a critical value.

2. The nucleation occurs in a very short time (10^{-6} seconds).

3. The nucleation stops abruptly because of the depletion of nucleating species from the growth of nuclei into viable particles.

4. The particles grow by physical condensation and agglomeration.

5. The first solid nuclei formed will be the equilibrium composition of solid particles formed. To achieve a complete reaction, the premature nucleation of condensed phases in the mixed regime must be avoided.

Figure 10 shows the thermodynamic equilibria of molten aluminum with 78% nitrogen and 22% oxygen, and the molar fractions of the products as a function of temperature. This situation approximated the conditions of the APS processing experiments. The equilibrium phases occur in three distinct regimes as temperature increased: compound stability, mixture of compound and reactants, and decomposition into elemental components. The compound stability regime for AIN occurs from 1000°C to approximately 1500°C, and the Al₂O₃ was calculated to be stable from 1000°C up to 3400°C. The mixed regime occurs for AIN from 1500°C to 3000°C with an equilibrium phase mixture of AlN, aluminum liquid, aluminum vapor and nitrogen. The Al₂O₃ mixed regime occurs over a narrower range between 3400°C and 4000°C by decomposing into aluminum vapor and dissociated oxygen. It was important to note, the decomposed regime occurs above 3000°C for AIN, and above 4000°C for Al₂O₃. This fact was important in the evolution of products from the APS processing. By referring to Figure 9 and following the cooling path from the vaporized species for the plasma experiments conducted in air, the condensed species forming between 2500°C to 3500°C would contain predominantly Al₂O₃ with aluminum and a small amount of AIN, which was observed in experiments 35 A-C. The amount of measured nitrogen increased only slightly comparing APS to CPS, when the oxygen was eliminated from the environment, and the plasma processing conditions held constant as in experiments 37 A-C. The small change occurred, because the condensation temperature still occurred at a similar temperature in the mixed stability regime of AIN above 2500°C.



Figure 10 - SOLGASMIX [20] Predicted Phase Equilibria for Plasma Spraying of Aluminum Powder in Air

The introduction of molten aluminum at 1000°C into plasma reduced the quenching effect of the surrounding environment and permitted the condensate to form at lower temperatures in mixed regime to increase the AlN content in experiments 133 B-C. Figure 10 shows a similar thermodynamic equilibria for molten aluminum and nitrogen gas from 1000°C to 5000°C. A slight difference exists between the spraying in air and the spraying in pure nitrogen with the decomposition of AlN beginning at a lower temperature, 1500°C versus 1700°C, in air due to the competing reaction with the more stable Al_2O_3 . The Mach I plasma and high metal flows in experiment 133D did not permit sufficient atomization, and therefore very little vapor was available to from AlN. The highest nitrogen pick up occurred in experiment 133A, because the vapor product was prevented from condensing until a temperature near 2000°C. The reduction in condensation temperature was believed to be a result of the plasma processing conditions, but the preheat serendipitously applied to the collection chamber was believed to be the dominant effect. If the interpretation of these results are correct, the 100% conversion of a high quantity of AlN powder should be easily accomplished with the Reactive Plasma Atomization process.





Potential Applications

The RPA process had the advantage of directly converting molten aluminum metal to AIN powder compared with a commercial processes. The commercial direct synthesis method uses air atomized powder with an aluminum oxide surface film, which requires reaction times of 2 - 3 seconds at temperatures from 1400°C to 1600°C [2]. The RPA apparatus is relatively simple, and could be easily large scaled to a manufacturing process with the incorporation of a melt tundish on top a typical commercial plasma gun. A wide variety of products can be produced depending on the process parameters and combinations of metal alloys and reactive gases. A low metal feed rate (15 g/min) and subsonic plasma is capable of producing a fully reacted powder (133-A), while a high metal feed rate (35 g/min) with a supersonic plasma can produce a spray formed deposit with a virtually no reaction (133-D). A partially reacted product can be collected as a composite powder or a spray formed composite tube or cylindrical billet. Alloy additions to the aluminum alloy, which are more thermodynamically stable may be selectively reacted to form a composite powder or spray formed product. For example, an aluminum alloy with 1 to 5% titanium could be reactive plasma atomized with nitrogen to produce an aluminum + TiN composite. If an alloy of AI-Si were RPA processed to full conversion, a new hybrid material (Al,Si), N, may be produced with better oxidation resistance and perhaps better mechanical properties. Although the emphasis of this investigation was the RPA processing of AlN powder, the RPA process may be used to produce other nitrides, carbides, borides and intermetallic compounds by introducing different molten metal alloys and reactive gases. Although the nozzle and crucible were fabricated from graphite in this investigation, they could be produced from any refractory material, such as alumina, magnesia, or zirconia, compatible with the chosen alloy system such as iron, copper, nickel, cobalt, magnesium, etc. There are a myriad of potentially useful combinations of alloys and nanophase reinforcements.

Conclusions

1. Reactive Plasma Atomization of molten aluminum produced conversion to a nanoscale powder which was 67% AIN with the remainder composed of predominantly metallic aluminum.

2. The feeding of molten aluminum permitted higher material processing rates than conventional powder feeding.

3. The degree of aluminum conversion to AlN was dependent on the efficiency of atomization and vaporization from the plasma parameters and the condensation temperature in the collector.

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