Heat Treatment of AA2024 Powders for Enhanced Solid State Structural Repairs via Cold Spray Deposition

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ABSTRACT

This presentation will describe new results on the heat treatment of AA2024 feedstock powder for cold spray deposition. Cold spray deposition is being developed as a means for repairing corrosion damage in high strength aluminum aircraft components. The microstructure of gas atomized powders is not optimized for spray characteristics or mechanical properties. We have applied a new heat treatment approach to solutionize these powders, thus removing the intermetallic network. Powders were solutionized for 75 minutes at 498°C in a rotary furnace and then quenched. For comparison, other powders were intentionally aged at 150°C and 225°C for 20 hours. All of these powders were sprayed onto AA2024 substrates using the VRC Metal Systems generation III cold spray system with helium as the spray gas. The mass deposition efficiency improved from 46% to 75% for the solutionized powders. The 150°C/20hour sample showed a reduction in deposition efficiency to 38%, while the 225°C/20hour sample increased to 61%. Microscopy of the particles showed that the solution treatment removed the majority of the S phase intermetallic network, while the overaging treatments did not. S' precipitates were not observed in coatings produced with feedstock powder but were present after natural aging for coatings produced with solutionized powders.

1. INTRODUCTION

Cold gas dynamic spray deposition, or "cold spray" is currently being developed for solid state structural repair (SSSR) of metallic components. In the cold spray approach to SSSR, small, metallic powder particles (5-40 µm in diameter) are accelerated to high velocities (e.g. 300-1200 m/s) before impacting onto a substrate using a supersonic gas jet at temperatures below the melting point of the feedstock material [1]. Cold spray has been successfully implemented for dimensional restoration of magnesium castings used in aircraft. Significant progress has been made in furthering the cold spray approach for structural repair including doubler repairs on F/A-18 aircraft. [2]

The rapid solidification processes used in the production of feedstock powders for cold spray produce undesirable microstructures for both the deposition and the deposited material's properties. The majority of powders for cold spray are produced using gas atomization, in which the cooling rates can reach 10^4-10^5 K/s. The atomization process will produce microstructures in a highly non-equilibrium state, typically possessing a network of intermetallics along cell or dendrite boundaries [3, 4]. The intermetallics are formed from solute atoms, which are thus unavailable for the formation of strengthening phases in heat treatable aluminum alloys. This cellular solidification microstructure with intermetallics distributed along the cell boundaries could also be detrimental to the ductility and perhaps also the corrosion resistance of the cold sprayed materials.

Post-atomization heat treatment of feedstock powders can mitigate the problems caused by the rapid solidification microstructure. To successfully remove the intermetallics, the material must be heated above its solvus temperature and then cooled rapidly enough to prevent the re-precipitation of the intermetallics. In addition, the powders must be prevented from oxidation and sintering during heat treatment. A number of authors have shown promising approaches to this problem. Y. She et al. [5] described a high temperature fluidized bed furnace for heat treating powders while avoiding sintering and oxidation of powders. Rokni et al. [6] used this fluidized bed approach for successfully heating treating AA5056 powders. They found that heat treatment of the powders enhanced the ultimate tensile strength and ductility in the resultant deposit. Sabard et al. [7] heat treated AA7075 powders by sealing the powders inside of a quartz tube and then heating the encapsulated powders inside of a commercial box furnace. Story and Brewer [8] recently demonstrated a powder heat treatment process for cold spray feedstock powders using a novel rotary, inert-gas furnace design, and this approach will be applied in this work. Implementation of a rotary vessel, back-filled with helium gas, prevented sintering and oxidation of powders. In addition, the vessel was quenched into a water bath to provide rapid cooling rate. In Story's initial results, the deposition efficiency of AA7075, AA6061, and AA2024 were all substantially improved by heat treatment of the feedstock powders. Furthermore, recent work by Liu, Story, and Brewer applied this approach to Al-Cu binary alloys containing 2-5 wt% Cu, and their results also show a systematic increase in deposition efficiency after powder heat treatment. [9]

This paper will build upon these recent papers and focus upon the effects of heat treatment upon AA2024 powders and its cold spray deposition. We will discuss the use of the rotary furnace for the heat treatment of AA2024 powders. We will show the changes in the micro- and nanostructures of the powders caused be the heat treatment. We will present data describing changes in the cold spray characteristics of these heat treated powders and describing the micro- and nanostructures of cold sprayed coatings made from these powders.

2. EXPERIMENTATION

2.1 Powder Heat Treatment

Powders were solution heat treated using a novel rotary tube furnace. Starting, inert gas-atomized powders of AA2024 (Al-4.4Cu-1.5Mg-0.6Mn in wt%) with an average diameter of 11.9 ± 7.1 μm were purchased from Valimet Inc. (Stockton, CA). Powders were heated for 75 minutes at a temperature 498°C ± 6°C, based on guidelines from the ASM Handbook Volume 4. During heating, the heat-treating vessel was rotated at a speed of 40 RPM and kept under an inert atmosphere of helium at +34.5 kPa (+5 psi). The delay between removal of the vessel from the furnace and quenching was not allowed to exceed 10 seconds. Rapid cooling of the powders (~50 °C/s) was accomplished by quenching the heat treating vessel into a brine bath.

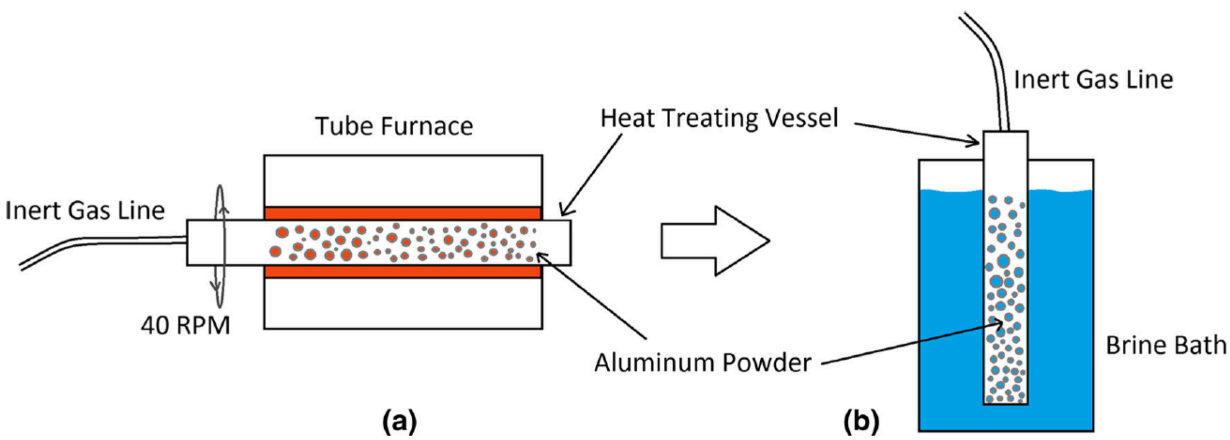

Figure 1. Schematic of rotary furnace for heat treating powder. (a) Powders are heated in an inert atmosphere while rotating the vessel to avoiding sintering during solution treatment. (b) Rapid cooling is accomplished by quenching the vessel containing the powders in a brine bath.

Because multiple heat treatment batches were necessary to produce enough powder for a cold spray run, powders were stored in a freezer at -20°C to prevent natural aging as additional powder was being produced. Powders described as "W Temper" were not allowed to experience room temperature for more than 30 minutes and were sprayed within 24 hours of solution heat treatment. One batch of solution heat treated AA2024 powder was allowed to naturally age for 170 hours prior to deposition.

2.2 Cold Spray Deposition

A series of four powders were cold sprayed using a VRC Metal Systems generation III instrument. In addition to solution heat treated powders (W Temper), as-atomized AA2024 powders were deposited for comparison. No special thermal processing was applied to these powders, but they were kept at room temperature for at least 3 months following gas atomization. AA2024 powders heated at 150°C and 225°C in a convection oven prior to deposition were also sprayed. AA2024-T351 plates (6.35 mm thick) were used for the substrates. Prior to deposition, the substrates were sanded with 60 grit SiC sandpaper and were then thoroughly degreased with a detergent and rinsed with isopropyl alcohol. The cold spray deposition was performed using a PBI nozzle with a 2 mm diameter throat, a 4 mm exit diameter, and a 120 mm length. Other cold spray parameters can be found in Table 1. Deposition efficiency was measured by measuring the mass of the substrate before and after deposition. The powder was weighed prior to spray deposition and then the mass of the remaining powder was measured. The % mass deposition efficiency (DE) is calculated as the ratio of the mass of material deposited onto the substrate to the mass of the powder used.

Spray Gas	93 volume % He/7 volume % N_2
Gun Temperature	415°C
Gas Pressure	3.21 MPa (465 psi)
Powder Feed Rate	40 g/minute
Standoff Distance	18 ±3 mm
Nozzle Traverse Speed	200 mm/s

Table 1. Cold spray deposition parameters.

2.3 Microstructural Analysis

Samples were prepared for microscopy analysis using a combination of standard metallographic techniques and focused ion beam methods. TEM samples from cold spray deposits were produced with as-received AA2024 powders and with solution heat treated AA2024 powders naturally aged for 170 hours following deposition. The TEM samples were prepared using a FEI Quanta 3D Dual Beam focused ion beam (FIB) instrument operated at 30 keV to produce thin sections approximately 15 µm long, 1 µm thick, and 5 µm deep. Subsequently, these foils were thinned to electron transparency using a Tescan Lyra FIB-FESEM operated at 30 keV and finally polished at 5 keV. TEM imaging and x-ray spectroscopy was performed using a FEI Tecnai F-20 Scanning/Transmission Electron Microscope ((S) TEM) with an EDAX energy dispersive x-ray detector operated at 200 keV. High angle annular dark-field (HAADF) imaging was used to map the distribution of solute atoms and precipitates in the samples.

The volume fraction of S phase present for AA2024 powders with different heat treatments was estimated using greyscale image analysis of backscatter electron (BSE) micrographs taken at 10,000x magnification. A JEOL-7000 FEG Scanning Electron Microscope (Akishima, Tokyo, Japan) was used to produce backscatter electron (BSE) micrographs. Ten fields-of-view were analyzed per condition. Because the spatial resolution using BSE imaging in the SEM is insufficient to detect nano-scale S' precipitates and GP zones, this method should only detect the S phase. In addition, greyscale image analysis of BSE micrographs was used to determine porosity of deposits. Twenty-five fields-of-view at 300x magnification were used for each reported value.

3. RESULTS

3.1 Powder Microstructure After Heat Treatment

BSE images of powder-particle cross sections clearly show the impacts of powder heat treatment upon particle microstructure. The as-atomized particle (Figure 2A) shows bright contrast at the cell boundaries due to segregation of Cu and Mg during rapid solidification. Heat treatment at 150°C for 20 hours (Figure 2B) further promotes the growth of this intermetallic network (likely S or θ phase). While we cannot view the nanoscale precipitates at this magnification, this 150°C/20 hour heat treatment should result in overaging of any precipitates in this particle microstructure. The heat treatment at 225°C for 20 hours (Figure 2C) shows similar changes to the intermetallic network. The solution heat treatment clearly changes the particle microstructure (Figure 2D). The intermetallic network has been removed from the particle. Some bright particles (Cu-rich) are still present, likely due to either incomplete heating of the particle or from re-precipitation of S or θ phase during cooling.

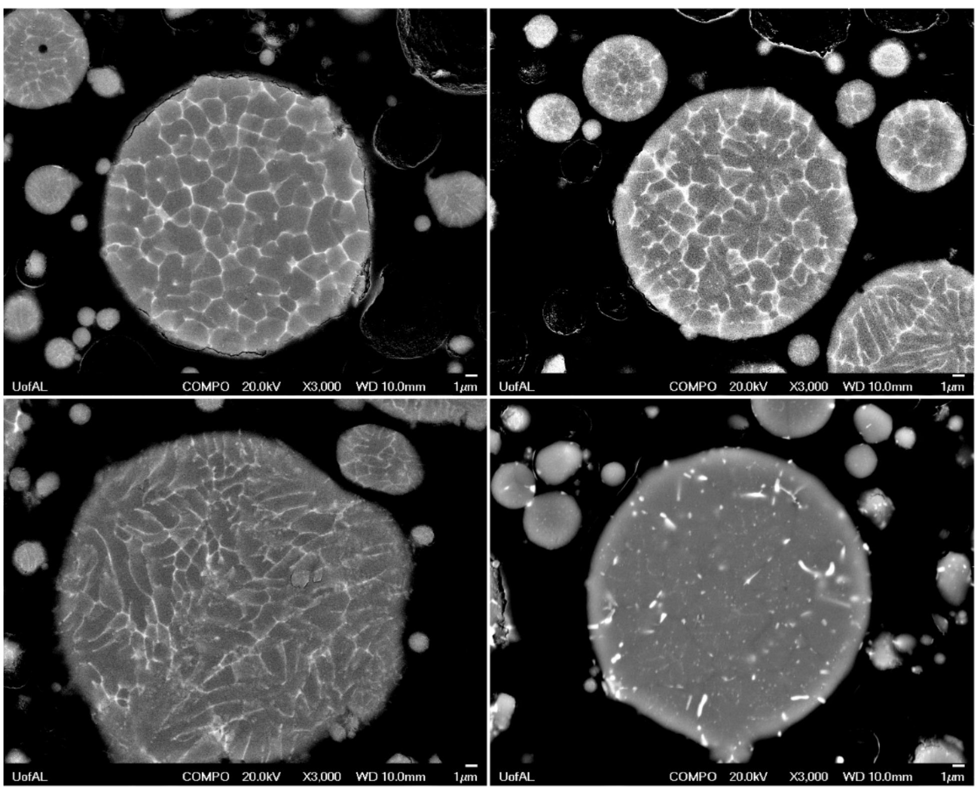

Figure 2. BSE micrographs of (A) as-received AA2024 powder (B) AA2024 powder heated at 150°C for 20 hours (C) AA2024 powder heated at 225°C for 20 hours (D) solution heat treated AA2024 powder.

3.2 Deposition Characteristics

Heat treatment of feedstock powder had varied effects on the cold spray deposition characteristics depending upon the temperature and times used (Figure 3). As-atomized powder resulted in a deposition efficiency of 46%. AA2024 powder solution heat treated showed a marked increase in deposition efficiency to 75% when sprayed in the W Temper condition. Interestingly, AA2024 powder that was solution heat treated and then and naturally aged for 170 hours at room temperature (T4 Temper) was observed to have a deposition efficiency of only 51%. This reduction in deposition efficiency is attributed to the strengthening of the powder due to the formation of nano-scale precipitates (e.g. G.P. zones or S") during natural aging. This natural aging has significant implications for the production, storage, and usage of solution heat treated powders, as low temperature storage may be required to prevent natural aging before deposition. This low temperature storage requirement is already implemented to maintain maximum formability of 2xxx series aluminum for applications such as rivets and aircraft wing plates [10]. The powders heat treated for 150°C for 20 hours showed a measurable decrease in deposition efficiency. This change is likely due to artificial aging of these powders, thus strengthening them. This reduction in DE is potentially concerning as aluminum powders are often dried in similar temperature-time ranges prior to cold spray. Operators will need to be mindful of the potential changes this drying process produces in the powders. Lastly, heat treatment at 225°C for 20 hours produced a substantial increase in DE. This change in DE is most probably due to over-aging of precipitates in the powder particles, thus softening the particles.

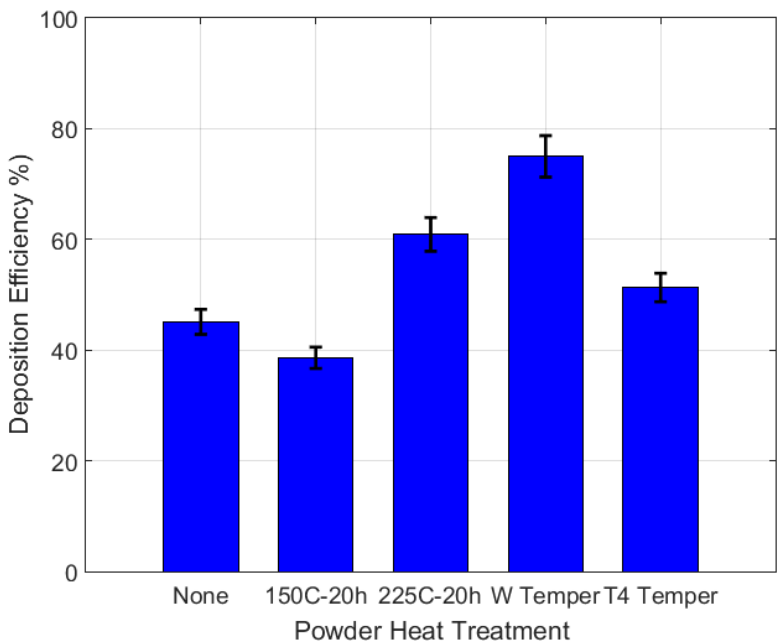

Figure 3. Deposition efficiency of AA2024 powders with different heat treatment conditions.

3.3 Coating Microstructure Using Heat Treated Powders

The distribution of intermetallics in cold sprayed coatings follows their presence or absence in the starting powders (Figure 4). The cellular microstructure is retained in coatings produced from as-atomized powders (Figure 4A). As expected, this cellular network is also retained, if not enhanced, in powders heated for 20 hours at 150°C (Figure 4B) and for 20 hours at 225°C (Figure 4C) prior to deposition. Powders with the W Temper produced a much more homogenous microstructure (Figure 4D). Likewise, natural aging of these powders following solution heat treatment (T4 temper, Figure 4E) also produced coatings without the intermetallic network. However, both the W Temper and T4 Temper coatings show particles with bright contrast due either to incomplete solutionization and/or insufficient cooling rate. In comparison, we should note that even in wrought 2024-T351, much larger, bright (higher atomic number) particles are present (Figure 4F). These particles are mostly S-phase with some Fe-rich intermetallics as well.

Solution heat treatment significantly reduces the volume fraction of the S-phase of the powder compared with as-received condition, but not quite to the level of commercial wrought AA2024-T351. Greyscale image analysis was conducted on BSE micrographs to quantify the extent to which full solutionization occurred (Figure 5). These percentages are only an estimate, and the brightness of each phase is related to its average atomic number compared with the aluminum matrix. In future work, x-ray diffraction will be used for a more precise measurement of phase fractions. Nonetheless, we do observe that lower temperature heat treatment (20 hours at either 150°C or 225°C) produced a greater volume fraction of the S-phase as would expect if over-aging is occurring. Clearly, the amount of micro-scale S-phase was much reduced in powders, which experience the solution treatment (W Temper). For comparison, the vol% of constituent particles in wrought material was even lower.

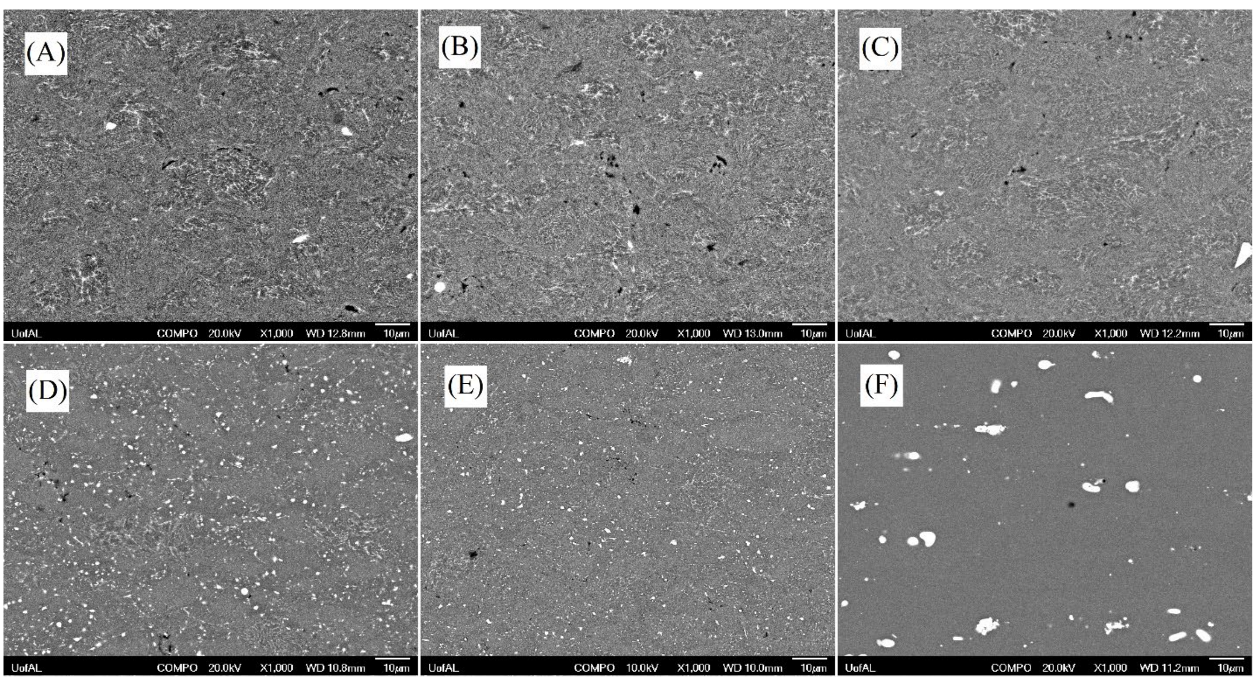

Figure 4. BSE micrographs of AA2024 cold spray deposits produced with (A) as-received powder (B) powder heated at 150°C for 20 hours (C) powder heated at 225°C for 20 hours (D) solution heat treated powder sprayed without allowing natural aging to occur and (E) solution heat treated powder sprayed after naturally aging for 170 hours. Wrought 2024-T351 is shown for comparison.

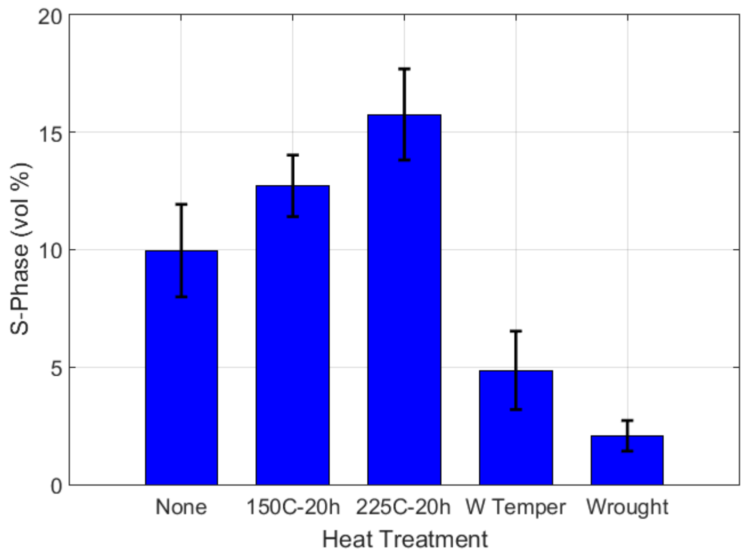

Figure 5. Volume fraction of the S phase present for different heat treatment conditions.

All cold sprayed deposits were measured to have a porosity of less than 0.5% (Figure 6). The deposits produced with aged powders exhibited significantly higher porosity than deposits produced with as-received powders. Deposits produced with solution heat treated powders exhibited slightly lower porosity than deposits produced with as-atomized powders, but they still exhibited significantly higher porosity than wrought 2024.

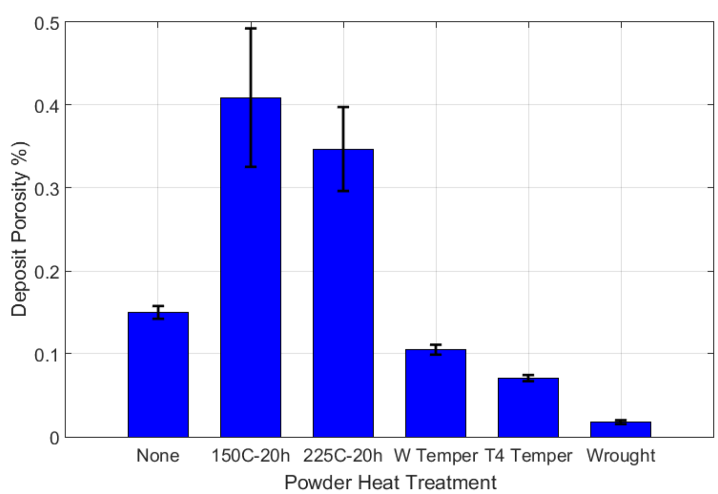

Figure 6. Cold spray deposit porosity for different heat treatment conditions.

STEM-HAADF imaging showed the effect of powder heat treatment on the nanoscale presence or absence of precipitates in cold sprayed coatings (Figures 7 and 8). Cold spray deposits produced with as-received powder showed no evidence of nanoscale precipitates or even G.P. zones (Figure 7A and C). While the lack of any precipitates, or even G.P. zones, may be surprising, a similar lack of nanoscale precipitates has been reported recently in the literature for as-atomized, binary Al-Cu powders [4]. This work did show that the aluminum matrix was enriched in copper by the rapid solidification process. In contrast, many, fine S' precipitates are observed in the cold spray deposit produced with heat treated powder (Figure 7 B and D). These precipitates exhibit a morphology characteristic of S' rather than θ' precipitates [11, 12]. X-ray maps from these regions confirm that these precipitates are rich in Al, Cu, and Mg (Figure 8).

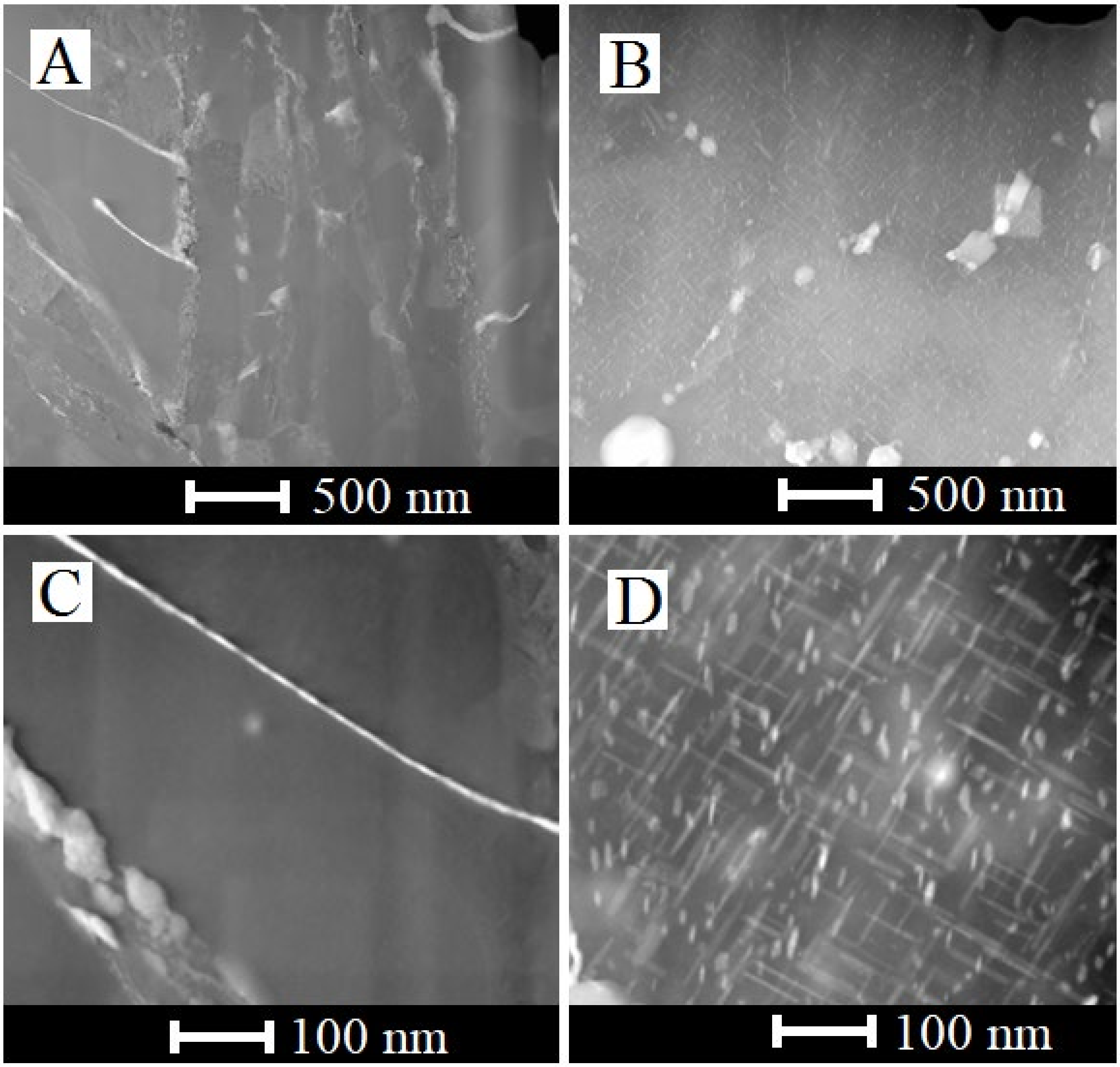

Figure 7. HAADF STEM micrographs of cold spray deposited material produced with as-atomized AA2024 powder (A and C, high and low magnification) and solution heat treated AA2024 powder (B and D, high and low magnification).

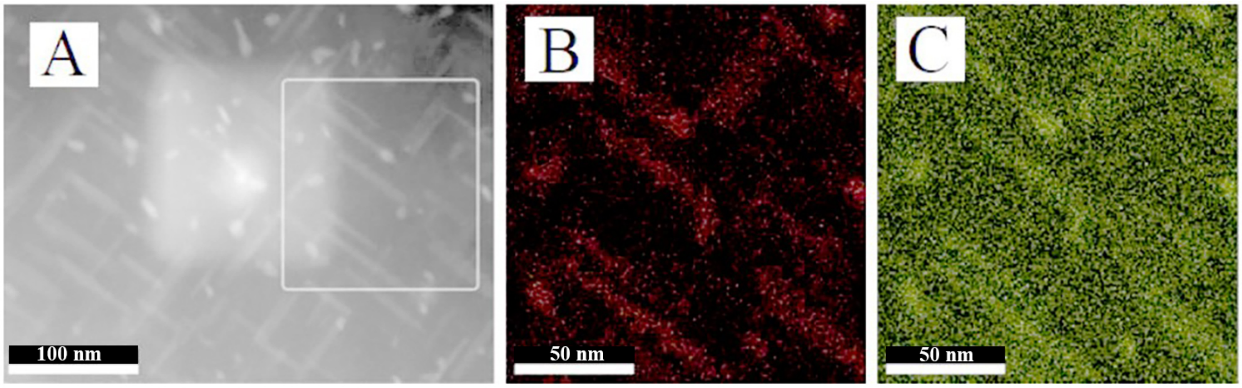

Figure 8. (A) HAADF STEM micrograph of cold spray deposited AA2024 that has been solution heat treated and naturally aged (approximately 170 hours). EDS was performed on the region indicated by the white box, showing that these precipitates are rich in magnesium (B) and copper (C).

4. CONCLUSIONS

- A novel rotary furnace has been developed to allow for solution heat treat of aluminum powders. This furnace avoids oxidation of powders by maintaining an inert atmosphere and avoids sintering by rotating the heat-treating vessel during heating. Particle quenching is accomplished by directly quenching the heat-treating vessel in water following solutionization.

- Solution heat treatment removes the majority of the intermetallic network produced during rapid solidification. Further improvements in uniformity of powder heating and in increased cooling rates during quenching will further complete the removal of intermetallics from the powder particles.

- Solution heat treatment significantly increased deposition efficiency of powders compared to as-atomized powders. However, it is also found that allowing these powders to naturally age in between heat treatment and deposition reduced deposition efficiency. Heating as-received powders at temperatures typically used to dry powders can result in either an increase or decrease in deposition efficiency depending on the time, temperature, and aging response of the powder.

- The micro- and nanostructures of coatings produced with heat treated powders were significantly altered by the heat treatment process. Cold spray coatings made with solutionized powders (W Temper) had far few microscale intermetallics than coatings made with as-atomized powder. In addition, coatings made with solutionized powders exhibited nanoscale precipitates (likely S' phase), while no nanoscale precipitates were observed in coatings made with as-atomized powders.

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