ABSTRACT

Spray forming is an advanced materials processing technology that converts a bulk liquid metal to a near-net-shape solid by depositing atomized droplets onto a suitably shaped substrate. By combining rapid solidification processing with product shape control, spray forming can reduce manufacturing costs while improving product quality. De Laval nozzles offer an alternative method to the more conventional spray nozzle designs. Two applications are described: high-volume production of aluminum alloy strip, and the production of specialized tooling, such as injection molds and dies, for rapid prototyping.

INTRODUCTION

Spray forming is an advanced materials processing technology that combines rapid solidification processing (RSP) with product shape control. The interaction of a high velocity gas jet with a liquid metal stream or sheet atomizes the metal, producing a spray of fine droplets that are deposited onto a substrate or pattern to form a near-net-shape solid. In an effort to simplify materials processing, lower costs, and improve product characteristics of high volume commodity shapes (e.g. tubular, billet, and sheet), various spray-forming approaches have been developed over the years. Examples include Liquid Dynamic Compaction, the Osprey process, and Consolidated Spray Deposition [1,2]. A versatile approach developed recently at the Idaho National Engineering Laboratory has been used to spray form metals, polymers, and metal matrix composites in near-net-shape and net-shape [3-9]. In this approach, a liquid is aspirated or pressure-fed into a de Laval (converging/diverging) nozzle. There it contacts a high velocity, high temperature inert gas that disintegrates the liquid into very small (~ 20 μm) droplets and entrains the droplets in a highly directed spray.

Spray deposition with de Laval nozzles typically involves transonic gas-particle flow through the nozzle and subsonic free jet flow from the nozzle to the substrate [10]. Laser Doppler velocimetry [11] has established that droplets are accelerated in the flow field to velocities of about 50 m/s. After exiting the nozzle, the spray jet rapidly entrains large volumes of relatively cold inert gas, which removes the liquid metal’s superheat and approximately 75% of the enthalpy of solidification. As a result, droplets arrive at the substrate in semi-solid, solid, and undercooled states depending on size.
and location in the flow field. Upon impacting the substrate, the droplets weld together, replicating the shape and surface texture of the substrate or pattern, while releasing the remaining enthalpy by convection and conduction through the substrate.

Properties of the deposit are tailored by controlling the characteristics of the spray plume (droplet size distribution, velocity, heat content, flux, and flow pattern) and substrate (material properties, surface finish, and temperature). Two applications are briefly described: high-volume production of aluminum alloy strip, and the production of specialized tooling, such as injection molds and dies, for rapid prototyping.

**ALUMINUM ALLOY STRIP**

Currently, about 80% of commercial aluminum sheet is produced by conventional ingot metallurgy (I/M) hot mill processing. Ingots are cast to thicknesses greater than about 400 mm (16 inches), scalped, homogenized, and hot rolled to form 2.5-6.4 mm (0.1-0.25 in.) thick coiled reroll stock. These "hot lines" are the starting point for a variety of commercial products [12]. In contrast, RSP by spray forming results in a homogeneous, refined microstructure that largely eliminates the need for hot rolling. The material is characterized by a refined, equiaxed grain structure with fine-scale, uniformly distributed constituent particles and the absence of macrosegregation. By reducing/eliminating the need for the intermediate hot rolling steps necessary with conventional I/M processing, energy savings and capital equipment cost reductions can be impressive for high volume strip sheet alloys. For example, a recent technoeconomic analysis estimated that energy savings of 15% are achieved by spray forming versus ingot casting with 10% overspray loss, and 27% savings are achieved with no overspray [13]. Net conversion costs for spray-formed sheet are about 13% lower than for conventional ingot casting/hot rolling assuming 10% overspray loss [13].

**Strip Preparation and Properties**

The apparatus used to produce aluminum strip has been described elsewhere [10]. The alloy to be sprayed is induction melted under a nitrogen atmosphere, superheated about 150°C, and pressure-fed into a de Laval spray nozzle of our own design. High-temperature, high-velocity nitrogen flow rapidly disintegrates the molten aluminum into fine droplets that are entrained by the jet in a directed flow and deposited onto a grit-blasted steel drum. An inert gas atmosphere within the spray apparatus minimizes slag formation in the melt and in-flight oxidation of the atomized droplets.

The nozzle is operated at a static pressure, measured at its inlet, of about 172 kPa absolute (25 psia). A gas-to-metal mass flow ratio (G/M) of about 0.3 is typically used, and metal mass flow rates are in the range 8,900 to 54,000 kg/h per meter (500 to 3000 lb/h per inch) of nozzle width transverse to the flow direction. This nozzle dimension is scaled for a desired strip width. To date, most experiments have been conducted using bench-scale (17 mm wide) nozzles. Currently, experiments are focusing on determining system scale-up rules and the effect nozzle scale-up has on strip profile, porosity, and yield.

Droplet flight times are on the order of milliseconds. Droplets impact the substrate, positioned about 0.3 m (12 in.) from the nozzle, producing a strip of metal 2.5-13 mm (0.1-0.5 in.) thick, depending on conditions. The transverse cross section of 6 mm (0.25 in.) thick 6061 aluminum strip shown in Figure 1 was spray formed with a bench-scale nozzle. A flat profile is critical for this application to prevent fracture during subsequent rolling operations. Transverse thickness is targeted at ± 2%. Overspray losses, defined as unconsolidated particulate and thin edge trimmings, are about 9% for bench-scale nozzles. Preliminary results indicate that overspray decreases as the nozzle is scaled-up.

Airborne spherical droplets cool by convection and radiation. The relative contribution of both cooling mechanisms depends on droplet temperature, Weber number, gas and droplet thermal diffusivity, and
other factors. Under most conditions, convection cooling strongly dominates. The cooling rate of droplets in 6061 aluminum spray jets was estimated by measuring the dendrite cell size in polished/etched powders. Powder was partitioned into size bands using sieves of 300, 212, 177, 149, 125, 75, 63, 45, 38, 25, 20, 15, 10, and 5 μm. In general, dendrite cell size increased with increasing powder size, consistent with previously published results on gas atomized aluminum alloys [14-18]. For example, the cell size increased from about 1.8 μm for a 20 μm particle, to about 9 μm for a 200 μm particle. Cell size was found to follow a power law relationship with powder size. Cooling rate was estimated from measured dendrite cell size using the relationship

\[ \lambda = Be^n \]

where \( \lambda \) is the average dendrite cell size, \( e \) is the cooling rate, and \( B \) and \( n \) are material and process dependent constants [14-18]. For aluminum alloys, they are typically about 50 μmK/s and 1/3, respectively, over the range 10\(^{-5}\) to 10\(^{6}\) K/s [14]. Cooling rates varied inversely with droplet size, ranging from about 10\(^{-2}\) to 10\(^{4}\) K/s, placing them well within the range of rapid solidification and at least one order of magnitude higher than the average cooling rate of the bulk deposit.

Discrete droplet impacts at the exposed deposit surface of 3003 aluminum strip in Figure 2 provide insight into the mechanism of equiaxed grain formation. Dendrites within the solidified particles are clearly visible in both photographs. Dendrite cells fragment after impact to provide a high concentration of nuclei which help refine the microstructure. The degree of droplet spreading in Figure 2a suggests a high droplet liquid fraction. Dendrite debris, fine-scale entrapped gas, and a high cooling rate at the surface may explain why coarsening is inhibited in spray-formed materials. The early stages of grain growth and coarsening are observed within two regions of the splat before the prior splat boundary has been erased. Equiaxed grain formation is at an advanced stage of development within one or two droplet diameters from the surface of the deposit. The droplet in Figure 2b exhibited low shear at impact suggesting a low liquid fraction.

Metallography of as-deposited 3003 aluminum indicates a refined equiaxed microstructure with good constituent dispersion and no macrosegregation. The photomicrograph in Figure 3a was taken near the center of a strip. The as-deposited bulk density, measured by water displacement using Archimedes’ principle, is 95 to 99.5% of theoretical density. Porosity in the samples is largely "cold" porosity and tends to be concentrated at the deposit/substrate interface. "Cold" porosity is formed when the liquid fraction of impinging droplets is insufficient to fill voids in the strip due to rapid quenching, rapid droplet arrest conditions. These conditions are favored at the substrate. "Hot" porosity, on the other hand, is characterized by circular pores formed by gas engulfment during solidification. Hot porosity was usually not observed. Efforts to reduce porosity in the strip near the deposit/substrate interface have been successful; the as-deposited photomicrograph in Figure 3b is an example. Depending upon conditions, average grain size is 15 to 50 μm for this alloy. Hot rolling at 450°C to 44% thickness reduction was found to reduce the average grain size by 25%.

Preliminary room temperature tensile properties were determined for spray-formed 3003 aluminum after tempering to conditions commonly available for commercial strip. As-deposited samples (without
scalping or machining) were hot rolled to 50% thickness reduction in a single pass, annealed, and cold rolled in one or two passes to yield -H14, -H16, and -H18 tempers. Results summarized in Table I compare commercial 3003 aluminum strip with these tempers [19] with as-deposited, unprocessed strip, and as-deposited strip (without scalping or machining) cold rolled to 50% thickness reduction. Ranges in spray formed values reflect differences in experimental conditions.

SPRAY-FORMED TOOLING

The conventional method for making specialized, custom tooling, such as injection molds and dies, involves machining the negative of the desired part shape (core and cavity) from a rough casting or a forged billet. Cooling channels/vents, etc., are machined, followed by grinding and polishing steps.
The process is very costly and time consuming, with lead times for an average mold of about three to six months. Tool checking and part qualification may require an additional three months. Tooling costs vary with size and complexity, ranging from $20K to over $200K. Lead times for large dies may be more than one year with costs exceeding $1M. Long lead times and high tool costs dampen innovation and result in only the most conservative concepts reaching the showroom or marketplace.

Spray-forming provides an alternative approach for tool making that combines RSP and net-shape materials processing into a single step. By so doing, unit operations in tool fabrication, such as machining and grinding, can be reduced or eliminated while simultaneously improving tool properties. Fine, atomized metal droplets are deposited onto patterns of wax, clay, plastic, ceramic, or metal. As
Table I. Tensile Propertiesa of Commercial 3003 Aluminum Alloy and Spray-Formed Strip

<table>
<thead>
<tr>
<th>Material/Temper or Condition</th>
<th>Ultimate Strength, MPa (ksi)</th>
<th>Yield Strength, MPa (ksi)</th>
<th>Elongation, %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial/ -O</td>
<td>97 (14.0)</td>
<td>34 (5.0)</td>
<td>25</td>
</tr>
<tr>
<td>Commercial/ -H14</td>
<td>138 (20.0)</td>
<td>117 (17.0)</td>
<td>5</td>
</tr>
<tr>
<td>Commercial/ -H16</td>
<td>165 (24.0)</td>
<td>145 (21.0)</td>
<td>3-4</td>
</tr>
<tr>
<td>Commercial/ -H18</td>
<td>186 (27.0)</td>
<td>165 (24.0)</td>
<td>2</td>
</tr>
<tr>
<td>Spray formed/ -H14</td>
<td>160.0-173.1 (23.2-25.1)</td>
<td>154.4-170.3 (22.4-24.7)</td>
<td>3.4-7.8</td>
</tr>
<tr>
<td>Spray formed/ -H16</td>
<td>195.5-198.6 (28.8-29.7)</td>
<td>188.2-195.5 (27.3-28.5)</td>
<td>3.0-6.8</td>
</tr>
<tr>
<td>Spray formed/ -H18</td>
<td>228.9 (33.2)</td>
<td>207.5 (30.1)</td>
<td>2.7</td>
</tr>
<tr>
<td>Spray formed/ as-deposited</td>
<td>129.3-135.1 (18.8-19.6)</td>
<td>86.2-102.2 (12.5-14.8)</td>
<td>9.5-14.6</td>
</tr>
<tr>
<td>Spray formed/ cold rolled 50%</td>
<td>190.8-194.4 (27.7-28.2)</td>
<td>186.2-188.1 (27.0-27.3)</td>
<td>5.0-5.2</td>
</tr>
</tbody>
</table>

a. Values for commercial sheet are minimum specification limits for sheet of comparable thickness to spray-formed sheet with the same temper.
b. For commercial material, % elongation is in 50 mm (2 in.) gage length. % elongation for spray formed samples is in 25 mm (1 in.) gage length.

the deposit builds up, it replicates the shape and surface texture of the tool pattern. The approach is compatible with rapid prototyping or solid freeform fabrication techniques such as stereolithography, laminated object manufacturing, and selective laser sintering that can produce tool patterns directly from CAD drawings.

Tool Preparation and Properties

The basic approach used to spray form tooling is similar to what is used to produce strip. However, different nozzle designs and operating parameters are used. Custom nozzle designs are operated at high gas-to-metal mass flow ratios to encourage the formation of fine droplets and a narrow range of droplet sizes. These conditions offer the greatest flexibility for controlling droplet temperature and liquid fraction, flow and momentum patterns of the spray, and, consequently, the microstructure.

A bulk liquid metal is aspirated or pressure-fed into a spray nozzle, atomized, and deposited onto a pattern that is manipulated in the jet to provide even coverage. Liquid metal and atomizing gas are heated to above the liquidus temperature of the alloy. Upon impact, the droplets spread and rapidly solidify. The deposit accurately replicates the shape and surface texture of the tool pattern. The resultant metal shell is cooled to room temperature and separated from the pattern.

Bench-scale nozzles have been operated at gas-to-metal mass flow ratios (G/M) as high as 10. Metal deposition rate is about 45 kg/h (100 lb/h) during the initial deposition stage as the pattern’s surface
features are replicated. Throughput is increased to as high as 900 kg/h (2000 lb/h) until the walls of the mold reached the desired thickness. A variety of commodity thermoplastics and advanced polymers have been used as pattern materials with good results, including low-density polyethylene (LDPE), polypropylene (PP), poly(methyl methacrylate) (PMMA), polycarbonate (PC), nylon 6/6, polystyrene (PS), polyetherimide (PEI), and polyimide (PI). Ceramic and metal tool patterns have also been used.

Examples of spray-formed mold shells are given in Figure 4. The alloy is a Zn-Al-Cu forming-die (Kirksite) alloy. Mold shells were produced in about 5 min with a bench-scale nozzle by spray depositing the metal onto LDPE patterns having the shape of sand toys. Replication of surface features, including fine scratches in the pattern, was excellent. Peak-to-valley surface roughness of the shells at the deposit/pattern interface was measured to be as low as about 5 μm using a stylus profilometer.

EDS analysis of the distribution and composition of the phases of Kirksite alloys indicated significant improvements in secondary phase dispersion, compared with cast material, due to rapid solidification. Solid solubility extensions were also observed in the spray-formed material. Oxide levels were lower than the detection threshold of the device. Figure 5a shows a photomicrograph of cast, equilibrium-cooled Zn-Al-Cu alloy. The same alloy spray formed at 52 kg/h (115 lb/h) is shown in Figure 5b. Figure 5c is a photomicrograph of the alloy spray formed at 470 kg/h (1033 lb/h). Photomicrographs of the spray-formed material illustrate morphological modifications due to RSP. Vickers hardness values of the spray-formed alloy of Figure 5b (92% dense) was 139, while the material in Figure 5c (98% dense) was 145. Hardnesses up to about 165 have been measured for the as-deposited material. These values compare favorably with the hardness of cast material (~120).

CONCLUSIONS

1. De Laval nozzle designs provide an alternative to conventional approaches to spray forming for a variety of applications.

2. Aluminum alloy strip was spray formed with flat profile, low porosity, and high yields. Technoeconomic analysis indicates the approach is competitive with continuous casting and hot mill processing of high volume sheet alloys. Refined, equiaxed grain structures and uniform distribution of
Spray formed at 52 kg/h (115 lb/h).

 Photonicrographs of etched Zn-Al-Cu alloy produced using a bench-scale de Laval nozzle.

Fine constituent particles and dispersoids are observed. Low porosity in the deposit at the deposit/substrate interface eliminates the need for scalping. Total elimination of porosity has not yet been achieved using a room temperature substrate. Tensile properties of spray-formed strip compare favorably with those of commercial strip for commodity aluminum alloys tested (3003 and 6061).

3. Processing parameters are being developed to spray form tooling for injection molding and stamping. Preliminary results indicate significant cost reduction and improved microstructural features due to RSP. High production rates are possible with excellent shape and surface feature replication using a wide variety of tool pattern materials. Processing limitations exist for some pattern materials and features including high-aspect-ratio features.
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REFERENCES


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