Spray forming is a near-net-shape fabrication technology in which a spray of finely atomized liquid droplets is deposited onto a suitably shaped substrate or mold to produce a coherent solid. The technology offers unique opportunities for simplifying materials processing without sacrificing, and oftentimes substantially improving, product quality. Spray forming can be performed with a wide range of metals and nonmetals, and offers property improvements resulting from rapid solidification (e.g. refined microstructures, extended solid solubilities and reduced segregation). Economic benefits result from process simplification and the elimination of unit operations. Researchers at the Idaho National Engineering Laboratory (INEL) are developing spray-forming technology for producing near-net-shape solids and coatings of a variety of metals, polymers, and composite materials. Results from several spray-forming programs are presented to illustrate the range of capabilities of the technique as well as the accompanying technical and economic benefits. Low-carbon steel strip >0.75 mm thick and polymer membranes for gas/gas and liquid/liquid separations that were spray formed are discussed; recent advances in spray forming molds, dies, and other tooling using low-melting-point metals are described.

LOW-CARBON STEEL STRIP

The National Critical Technologies Panel recently determined that materials processing is a leading critical technology for meeting future national needs [1]. Spray-forming technology may help address these needs by improving product quality while simultaneously lowering production costs. Nearly all low-carbon steel strip is produced by conventional ingot or thin-slab metallurgical techniques. The molten steel is cast as an ingot or slab and extensively deformed to obtain the desired shape and properties. This is highly energy intensive and requires large capital investments. In contrast, INEL spray-forming technology transforms molten metal to close to final strip form in a single rapid solidification step. Minor hot rolling then fully densifies and further refines the metal's microstructure. This can lead to enormous cost savings. For low-carbon steel hot band, the industry's highest volume commodity, technoeconomic analysis estimated improvement in production costs by as much as $50 to 100 per ton. At the current domestic production rate of 50 to 60 million tons per year, this corresponds to cost savings of $2.125 to 6 billion per year. This savings, due primarily to elimination of unit operations and associated energy costs, would give the United States a tremendous competitive advantage in low-carbon steel production. Improvements in product quality are equally impressive. For example, after hot rolling (~60% thickness reduction), INEL spray-formed low-carbon steel strip typically had about 50% higher yield and ultimate tensile strength than commercial strip, i.e., its properties resemble those of the more costly high-strength low-alloy steels. Furthermore, spray forming may be an enabling technology for metals such as high silicon steels that are prone to segregation, which leaves the material too brittle to roll into strip. Rapid solidification in spray forming limits segregation and may allow these materials to receive conventional thermomechanical treatments.

Strip Preparation

The INEL spray-forming approach for producing metal strip is depicted schematically in Figure 1. Gas flow through a converging-diverging (de Laval) nozzle creates a localized low-pressure region near the
Figure 1. Schematic of INEL approach for spray forming metal strip.

The spray apparatus has been described previously [2]. The design is modular, allowing experimental flexibility for scale-up or the incorporation of specialized components such as a plume diagnostics unit. The apparatus used for continuous strip production consists of a gas manifold and associated electronics for controlling gas flow and temperature, a chamber housing the main spray forming components (induction gas heater, melt tundish, and nozzle), a chamber housing the water-cooled drum substrate, and data acquisition and process control electronics. Process control includes open- or closed-loop computer control of the spray process, laser-based feedback control of strip thickness and surface roughness, and remote video monitoring of the spray process. An in-flight particle diagnostics system is used to simultaneously measure single particle size, velocity, and temperature in the atomized plume. This system measures particle diameters between 5 and 1000 μm using an absolute magnitude of scattered light technique. Velocities of 10 to 100 m/s are measured with a dual beam laser Doppler velocimeter, and particle temperature is measured with a high-speed two-color pyrometry technique.

Bench-scale linear converging/diverging nozzles of our own design were machined in-house from boron nitride. Interchangeable inserts of high purity Al₂O₃ were used in critical areas to minimize erosion of the boron nitride by the molten steel. The throat width, transverse to the direction of flow, was about 25 mm. Mass throughputs were as high as 43 Mg/h per meter of slit width for a slit orifice nozzle operating in the aspiration mode, and 165 Mg/h·m for the same nozzle operating in the pressurized feed mode. A purged argon atmosphere within the spray apparatus minimized slag formation in the melt, surface oxidation of the strip, and in-flight oxidation of the atomized droplets.

The nozzle operated at a static pressure of 206 kPa (30 psia) absolute, measured at the nozzle's inlet. The gas flow field under single-phase flow conditions was mapped using small pitot tube probes. The driving pressure was found to generate supersonic flow conditions; the shock front was in the diverging section near the metal feed location. Gas-to-metal mass ratios typically ranged from 0.1 to 0.5. The gas...
and droplet cooled rapidly after exiting the nozzle as the spray plume entrained cool ambient argon. Gas and droplet velocity also decreased after exiting the nozzle, with large droplets responding less to drag effects by virtue of their greater momentum.

The starting material was remelted SAE 1008 hot band. During a typical run, 1.5 kg of steel was induction heated to about 100°C above the liquidus temperature and atomized using argon heated to about 1000°C. The resultant droplets impacted a water-cooled, grit-blasted mild steel drum, producing a strip of metal about 127 mm wide x 3 mm thick.

**Spray-Formed Strip Properties**

The microstructure of the as-deposited steel was usually fine, equiaxed ferrite with 11 to 45 μm average grain size. The transformation of the microstructure of SAE 1008 steel as it goes from commercial hot band to as-deposited material and finally to hot-rolled product is shown in Figure 2. Note that the average grain size of the as-deposited material is about the same as that of the commercial hot band (-16 μm), but the grains are somewhat more directional, reflecting the heat transfer direction. The grain structure of the spray-formed and hot-rolled material was equiaxed ferrite with -5 μm grain diameters.

As-deposited density, measured by water displacement using Archimedes' principle, ranged from 88 to 97% of theoretical density with 96% being typical. Full densification of the as-deposited strip was achieved with standard hot deformation processing. Depending upon the sample, hot rolling at 1000 to 1100°C to 30 to 70% thickness reduction was sufficient. Porosity in the as-deposited material was generally highest at the substrate due to high initial quench rates (10⁴ to 10⁸°C/s) [3-6]. Thin deposits formed from low density sprays had the highest porosity levels, but also finer grains due to rapid solidification. Low porosities together with fine microstructures were obtained with conditions that favored the formation of dense sprays consisting of small droplets with low solid fractions. The refined and uniform microstructures of thin hot-rolled strip generated under these conditions can be seen in Figure 3. Thick samples (>9 mm) formed from high enthalpy plumes also had lower porosity levels but coarser as-deposited microstructures. Hot rolling to 35% thickness reduction at 1000°C produced a fine equiaxed ferrite grain structure with an average grain size similar to commercial hot band material. A photomicrograph of strip formed under these conditions, as well as one for commercial hot band, is shown in Figure 4.

As expected, the tensile properties of the spray-formed and hot-rolled low-carbon steel strip reflect the observed grain refinements. Table 1 summarizes the results. The range of values arises from differences

![Figure 2](image-url)  
**Figure 2.** Microstructures of commercial SAE 1008 hot band (left), as-deposited spray-formed strip (center), and hot-rolled spray-formed strip (right). 400X

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in processing parameters (particularly spray conditions). Compared to commercial hot band, yield strengths increased 47 to 64% and ultimate strengths 9 to 63%. The observed reduction in elongation was largely restored by normalizing the samples (heating to 930°C for ~5 min followed by air cooling). Fully annealed samples (heated to 930°C followed by very slow cooling in the furnace) underwent the expected grain growth, with a notable decrease in tensile strength and hardness, and an increase in ductility.

POLYMER MEMBRANES

The unique capabilities of polymer membranes in a wide variety of gas/gas and liquid/liquid separations is well established [7]. The transport properties depend on the membrane’s microstructure or “fabric” as well as the physicochemical properties of the polymer and the operating conditions [8]. The microstructure, in turn, is dictated by the fabrication method. The need to fully exploit the potential of existing membrane materials through performance-enhancing fabrication techniques is underscored by the increasingly stringent requirements for air and water purity and waste minimization (see, for example, Title 1 of the Clean Air Act) [9]. To this end, spray forming technology developed for metal coatings was adapted to polymer membrane fabrication. Membranes were spray formed from poly[bis(phenox)phosphazene] (PPOP), an inorganic polymer exhibiting exceptional stability in the adverse thermal (>100°C) and chemical (extreme pH) environments frequently encountered in industrial separations [7]. The gas/gas and liquid/liquid separation performance of spray-formed membranes compared favorably with that of similar membranes produced by the conventional method of evaporative knife-casting [10].

Membrane Preparation

Membranes were formed by depositing atomized droplets of linear PPOP dissolved in tetrahydrofuran (THF) onto glass substrates using a bench-scale apparatus developed for spray forming metal. The
Figure 4. Microstructure of SAE 1008 steel hot band (left) and thick (> ~9 mm) spray-formed and hot-rolled strip (right). 100X

Table 1. Tensile Properties of Commercial SAE 1008 Hot Band and INEL Spray Formed and Hot Rolled Strip.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield Strength 0.2% Offset, MPa (ksi)</th>
<th>Ultimate Strength, MPa (ksi)</th>
<th>Elongation, % in 50 mm</th>
<th>Hardness, DPH 100 g Loads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial 1008 Hot Band</td>
<td>197 (28.6)</td>
<td>306 (44.4)</td>
<td>51.8</td>
<td>91</td>
</tr>
<tr>
<td>Spray Formed and Hot Rolled</td>
<td>290-324 (42.0-47.0)</td>
<td>334-498 (48.4-72.3)</td>
<td>13.9-37.7</td>
<td>136-160</td>
</tr>
</tbody>
</table>

chemical stability of the polymer allowed the membranes to be sprayed in air; argon was the atomizing gas. The linear converging-diverging (de Laval) nozzle, designed at INEL, was machined from boron nitride.

A 7 wt% solution of linear PPOP in THF was sprayed. The weight average molecular weight of the polymer, measured by gel permeation chromatography, was about 750,000 amu. (3 and 5 wt% solutions having polymer weight average molecular weights exceeding one million amu were also sprayed but gave less satisfactory results.) The solution was warmed to ~45°C to lower its viscosity and poured into the tundish of the nozzle, which operated at a static pressure of 137 kPa (20 psia). The solution was aspirated through six small orifices that spanned the width of the nozzle. Solution throughput was about 0.4 kg/s per meter of nozzle throat width. The corresponding gas-to-polymer-solution mass ratio was about 4. The solution was sheared and atomized, resulting in very fine droplets that were entrained by the gas stream and transported to a moving substrate. Solvent molecules were shed from the atomized droplets during their flight, and the remainder evaporated at the substrate. While control of atomizing gas temperature
could be a convenient means of adjusting the solvent evaporation rate, room temperature argon was used because the equilibrium vapor pressure of THF (145 torr at 20°C) is high enough to allow facile evaporation of the solvent. Upon impact, individual polymer molecules within adjacent droplets interwove while shedding any remaining solvent.

The polymer/solvent spray was deposited onto 8.3 x 8.3 cm glass plates, maintained at room temperature, that were swept through the spray plume at rates yielding membranes 1 to 10 μm thick. A typical 5 μm thick membrane was fully dried and consolidated in about 1 s. The membranes appeared to be coherent and uniform and exhibited good adhesion to the substrate. SEM analysis revealed an asymmetric structure as described below.

The hydrophobic membranes were lifted from the substrate by water immersion, mounted onto a porous test cell support, and edge-sealed using polymer solution. Knife-cast membranes prepared using a standard approach were also floated off their glass substrates into water and mounted onto test cell supports.

Membrane Characteristics and Performance

The microstructure of the spray-formed PPOP membranes was dictated by the interplay of the spray plume and substrate. Experimental parameters such as nozzle geometry and pressure, average molecular weight of the polymer, viscosity and concentration of the polymer solution, evaporation rate of the solvent, and distance to the substrate had the greatest affect on the spray plume characteristics. The speed, temperature, and properties of the substrate also influence the membrane's microstructure.

Scanning electron microscopy (SEM) was used to evaluate membrane surface structure and thickness. Over the width of the glass plates, the membranes appeared homogeneous and of uniform thickness. Close examination revealed that the membranes were asymmetric, with a thin, dense region at the substrate/polymer interface and a relatively thick, uniform build-up of translucent, "spongy" polymer material away from the substrate. Knife-cast membranes, on the other hand, appeared more uniformly dense and transparent.

Gas selectivity was measured using a fully automated mixed gas test cell interfaced to a Hewlett Packard 5190 gas chromatograph [11]. Pervaporation studies were conducted at 65°C using a driving pressure of 200 psig across the membranes. The selectivity of spray-formed and knife-cast PPOP membranes was determined for several acid gas mixtures (10% SO₂/90% N₂, 10% H₂S/90% CH₄, 10% CO₂/90% CH₄). SO₂/N₂ mixtures are encountered in industrial exhaust while H₂S/CH₄ represents well gas. The results are given in Table 2. At 80°C, spray-formed membranes had 4 times the selectivity of knife-cast membranes when separating SO₂ from nitrogen; at 130°C the difference increased to about 42 times. Spray-formed membranes had twice the selectivity of similar knife-cast membranes when separating H₂S from methane at 80°C and had 67 times the selectivity at 130°C. Improvements were also observed with spray-formed membranes when separating CO₂/CH₄ mixtures.

Spray-formed membranes also performed impressively in certain liquid/liquid separations. In pervaporation experiments, spray-formed membranes gave excellent component separation for a mixture of halogenated hydrocarbons and alcohols in water (0.5% methylene chloride, 0.5% chloroform, 0.5% methanol, 0.5% ethanol, 98% water). The alcohol-rich permeate (41.8% ethanol, 58.2% ethanol) contained a trace amount of water. The halogenated hydrocarbon concentration in the permeate was extremely low--below the detection limit in gas chromatographic analysis. Knife-cast membranes gave similar results. However, the flux through spray-formed membranes (2.83 L/m²-h) was appreciably higher than that through knife-cast membranes (0.1-0.4 L/m²-h) of the same thickness tested under the same conditions.

Membrane fabrication via spray forming offers time savings, flexibility, and improved performance over traditional approaches (e.g. knife casting or spin casting). Whereas knife-cast membrane preparation
Table 2. Component Selectivity Data for Spray-Formed and Knife-Cast PPOP Membranes.

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Temperature (°C)</th>
<th>PPOP Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% SO₂/90%N₂</td>
<td>80</td>
<td>71:1</td>
</tr>
<tr>
<td>10% H₂S/90% CH₄</td>
<td>80</td>
<td>15:1</td>
</tr>
<tr>
<td>10% CO₂/90% CH₄</td>
<td>80</td>
<td>4.5:1</td>
</tr>
<tr>
<td>10% SO₂/90% N₂</td>
<td>130</td>
<td>7.2:1</td>
</tr>
<tr>
<td>10% H₂S/90% CH₄</td>
<td>130</td>
<td>5:1</td>
</tr>
</tbody>
</table>

required hours, spray-formed membranes were prepared in seconds. The flexibility gained by spray forming membranes to near-net shape not only greatly reduces production costs by eliminating unit operations, but also allows membranes with complex shapes, which are difficult or impossible to manufacture by conventional approaches, to be produced in a straightforward manner. The ability to tailor membrane microstructure to specific separation processes by varying the spray and substrate parameters mentioned previously enhances performance.

SPRAY-FORMED TOOLING

The recent explosion of interest in rapid prototyping technology is fueled in part by the restructuring of today's marketplace. Successful competition in global markets will require the ability to carry a design concept through the prototype stage to the production stage faster and at lower cost than ever before. The ability to generate plastic and wax models of prototype parts with high dimensional accuracy via selective laser sintering [12], stereolithography [13], ballistic particle manufacturing [14], and other approaches is now a reality. However, it is generally accepted that the rapid production of prototype parts from engineered materials--materials that will actually see service--is the prime long term goal [15]. Methodologies that can rapidly produce specialized tooling, such as molds and dies, would satisfy this goal when used with conventional approaches such as injection molding, compression molding, and die casting.

Presently, complex molds, dies, and related tooling are expensive and time consuming to make. They can easily exceed $200K in cost and require months to fabricate. Researchers at the INEL have recently begun to develop spray forming technology to produce specialized tooling by spray depositing molten metal droplets onto patterns made from plastics, waxes, clay, or other easy-to-form materials. This approach could provide a unique opportunity for simplifying production of complex tooling, thereby substantially reducing its cost. Rapid solidification enables patterns made from plastics, waxes, clays, etc. to be used despite their low softening temperatures, while near-net-shape capability allows objects with complex shapes to be made easily. The semispherical shell shown in Figure 5 was generated by spray depositing molten tin directly onto an inflated party balloon.

Experimental

To form a mold, die, etc., liquid metal was pressure fed into a venturi-like nozzle transporting high velocity (mach number ~1.5) argon at temperatures above the liquidus temperature of the metal to be sprayed. Kinetic energy transfer from the gas overcame the relatively strong surface tension forces of the liquid metal, resulting in finely atomized metal droplets. The droplets were entrained in a directed two-phase flow, quenched, and deposited onto a moving plastic pattern having the desired shape and surface texture. The main spray-forming components (spray nozzle, liquid metal reservoir, gas heater, and pattern)
Figure 5. Party balloon spray-coated with tin emphasizes rapid solidification and near-net-shape capability of spray forming.

were housed in an argon-purged chamber to limit the detrimental effects of oxide formation. All spray components were designed and constructed in-house.

The nozzle/metal feed assembly was designed to produce sprays of relatively fine droplets having a narrow size distribution. These conditions offer greater flexibility for controlling droplet temperature, momentum, and flow pattern, as well as deposit microstructure. Bench-scale nozzles having transverse throat widths of 17 mm were typically operated at gas-to-metal mass ratios (for tin) of about 10 with metal throughputs of about 0.5 kg/s per meter of nozzle throat width.

Single-phase gas flow field diagnostics were used to map the static pressure and gas velocity profiles within the nozzle's flow channel. Size analysis of solidified droplets was conducted using standard wet and dry sieving methods.

A quasi one-dimensional computer model was used with the diagnostics results to guide component optimization as well as development of algorithms for process control. The model simulated the entire nozzle and free jet (plume) regions with full aerodynamic and energetic coupling between the metal droplets and the transport gas, and with coupled liquid injection into the gas stream.
Results and Discussion

The ultimate goal is fabrication of complex tooling from tool forming and hardfacing stainless steel alloys and composite materials. At the time of this publication, however, development of spray-forming tooling at the INEL is in its early stages. Several low-melting point alloys of zinc and tin have been tested with very encouraging results. An example is given in Figure 6, which shows a metal mold produced in about 5 min by spray-forming molten tin on a plastic (low-density polyethylene) pattern having a butterfly shape. The pattern was not damaged despite the fact that the temperature of the molten metal within the crucible (300°C) greatly exceeded the melting point of the pattern (100°C). Replication of surface features, including fine scratches in the pattern, was excellent. The surface of the mold was mirror-like and free of solidification shrinkage defects, indicating that replication of the pattern's surface texture was very good. Patterns of a variety of other plastics, including acrylic, polycarbonate, and polystyrene, have also given good results.

A photomicrograph of a sectioned mold, given in Figure 7, illustrates the refined grain structures that can be obtained using this rapid solidification process. The as-deposited grain structure was equiaxed with a fairly narrow range of fine (~6-16 μm) grain sizes—much finer than the massive grains found in cast objects. As-deposited density, measured by water displacement using Archimedes' principle, was typically 88 to 95% of theoretical.

The molten metal used to produce the deposit was very finely atomized. Unconsolidated powder was collected and analyzed by wet and dry sieving through fine mesh screens. The mass median diameter, volume mean diameter, and Sauter mean diameter of the powder were, respectively, 23 μm, 31.3 μm, and 23.2 μm. The geometric standard deviation (σg = (d84/d16)1/2 as determined from a log-normal plot) was 1.5, indicating a narrow droplet size distribution in the spray plume. SEM analysis revealed that nearly all the particles were spherical.

An important advantage of spray forming molds, dies, etc., is the ability to use patterns made from easy-to-shape materials such as plastic, wax, or clay, even though the softening point of these materials may be well below the crucible temperature of the molten metal. Since plastic and wax prototype models can now be produced using CAD-based systems, spray forming could develop into a complementary approach for generating specialized tooling for manufacturing prototype parts from engineered materials. The reduced time and cost of these molds/dies would allow rapid design verification and enable new designs and technology to enter the marketplace more quickly.

ACKNOWLEDGMENTS

We gratefully acknowledge significant contributions of Ray Berry in modeling multiphase flow behavior, heat transfer, and solidification phenomena; Denis Clark in substrate development, process control, and modelling efforts in spray deposition; James Fincke and David Swank in particle and gas flow field diagnostics; and Eric Peterson in membrane characterization and testing. This work was supported by the U.S. Department of Energy, Office of Conservation and Renewable Energy, Office of Industrial Technology, and by the EG&G Idaho Laboratory Directed Research & Development Program under DOE Idaho Field Office Contract DE-AC07-76ID01570.
Figure 7. Microstructures of cast tin (left) and spray-formed tin mold of Figure 6 (right). 400X

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