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Use of de Laval Nozzles in Spray Forming*

K.M. McHugh and J.F. Key

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 pattern to produce a coherent solid. The technology offers unique opportunities for simplifying materials processing, often while substantially improving product quality. Spray forming is applicable to 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 using de Laval nozzles. This article briefly describes the atomization behavior of liquid metals in linear de Laval nozzles and illustrates the versatility of the process by summarizing results from two spray forming programs. In one program, low-carbon steel strip >0.75 mm thick was produced; in the other, polymer membranes ~5 μm thick were spray formed.

1. Introduction

CONVENTIONAL metal spray forming nozzles atomize a stream of liquid metal issuing from the base of a crucible using a concentric array of gas jets. The resultant shower of droplets impinges on a moving substrate and forms a solid deposit. Spray forming with de Laval (converging/diverging) nozzles involves a close-coupled atomization technique (Fig. 1). Liquid metal is aspirated or pressure-fed into the nozzle flow channel, where it contacts a high-velocity, high-temperature inert gas that disintegrates the liquid into fine droplets. The gas stream entrains the droplets in a highly directed spray. Although this approach is inherently somewhat more complicated than the conventional approach, it can offer unique benefits.

De Laval spray forming nozzles can be classified as fully closed atomizers with internal mixing following the description given by Carbonara.[1] or as plain-jet "airblast" spray nozzles following the classification scheme of Lefebvre.[2] Spray deposition with these nozzles typically involves transonic gas-particle flow through the nozzle and subsonic free jet flow from the nozzle to the substrate. A pressure gradient is used to introduce liquid into the gas flow channel, which can be circular in cross section in the direction transverse to the flow, or "oval" if a broad spray pattern is desirable. The latter is referred to as a "linear" nozzle and is particularly well suited for applications such as strip production where the width of the nozzle is scaled according to the desired strip width. Metals, polymers, and composite materials have been spray formed by feeding the liquid through a slit orifice or a series of circular orifices that spans the width of the "linear" nozzle. For metals, in-flight convection cooling of the droplets followed by conduction and convection cooling at the substrate results in rapid solidification of the deposit. This restricts grain growth and improves product homogeneity by reducing the segregation of impurities. The shape of the spray-formed object is largely dictated by the geometry of the substrate or pattern onto which the spray is deposited, allowing complex shapes to be readily produced.

The properties of the spray-formed product reflect the interplay of the characteristics of the spray plume (droplet size distribution, velocity, heat content, flux, and flow pattern) and substrate (material properties, surface finish, and temperature). Consequently, an understanding of the atomization behavior of the liquid and of the characteristics of the multiphase flow fields both inside the nozzle and in the free jet regions is important for controlling the properties of the spray-formed product. Selected results from liquid metal atomization studies of linear de Laval spray forming nozzles are described below, followed by a brief summary of results from two spray forming programs.

Keywords: de Laval nozzles; microstructure; particle morphology; polymer membranes; spray forming

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2. Liquid Metal Atomization in Linear de Laval Nozzles

During gas atomization, a liquid is disintegrated into fine droplets by aerodynamic forces that overcome the surface tension forces acting to consolidate the liquid. The liquid viscosity and density also influence atomization behavior, but typically play a secondary role. Viscosity affects the extent of atomization as well as the resultant spray pattern by influencing the inter-

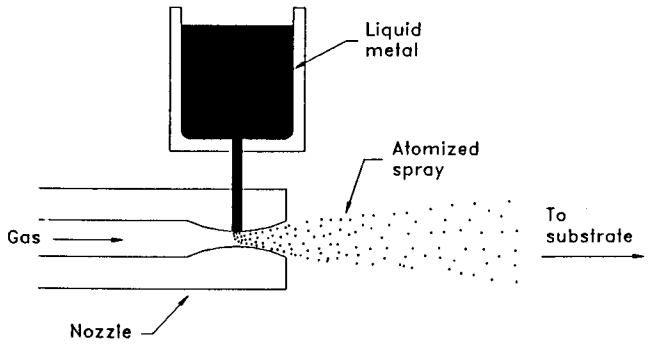
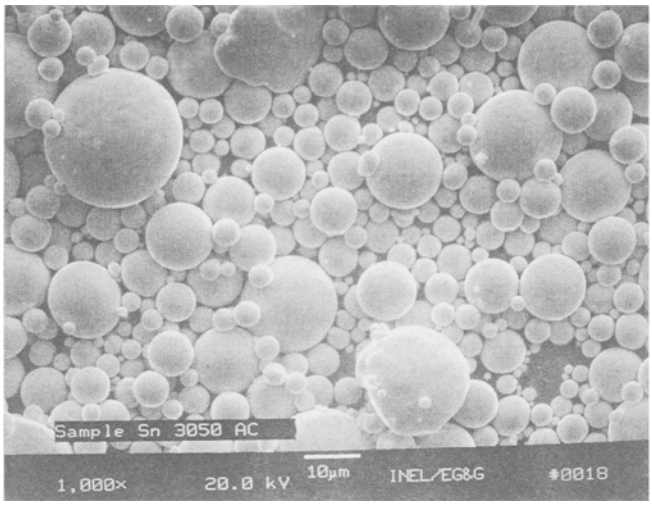


Fig. 1 Schematic of spray forming approach.



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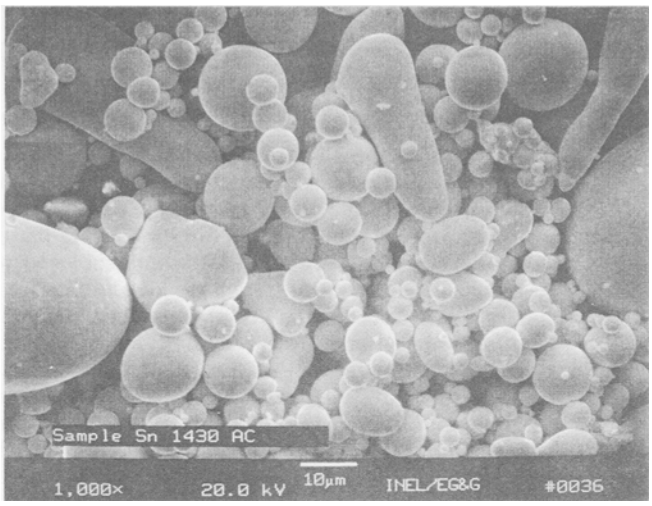

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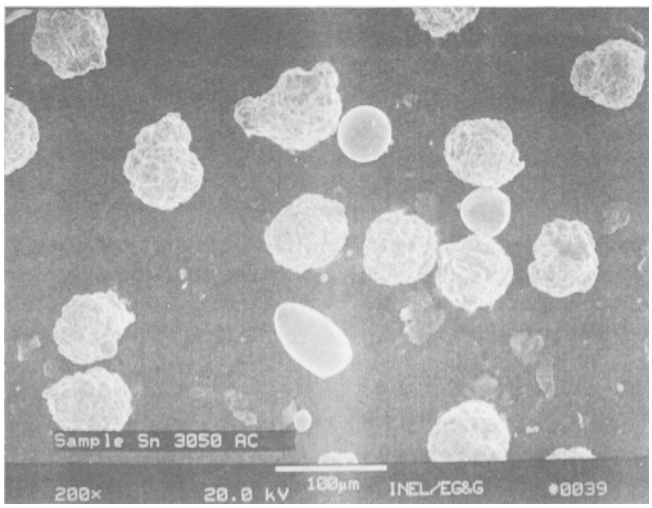


(c)

Fig. 2 SEM photographs of tin produced under various nozzle flow conditions. (a) normal spherical or near-spherical particles formed at high flow rates. (b) intermixed prolate ellipsoidal and fine spherical particles formed at moderate flow rates. (c) irregular powder shapes formed at low gas flow rates.

facial contact area between the liquid and gas. Viscous liquids oppose change in geometry more effectively than low viscosity liquids, making the generation of a uniform spray jet more difficult for a given set of flow conditions. Density influences the liquid response to momentum transfer from the gas. Light liquids accelerate more rapidly in the gas jet; disintegration efficiency is reduced because atomization takes place at lower relative velocities.

Liquid metals are characterized by moderately high viscosity, high density, and very high surface tension compared to common liquids such as methanol, water, and acetone. Atomization is more difficult with liquid metals than with most liquids due to the combination of these properties and their intrinsic high-temperature requirements. Thus, liquid metal spray forming nozzles need to be designed to provide good gas/metal coupling with efficient kinetic energy transfer from the gas. In linear de Laval nozzles, the liquid metal enters the flow channel with an axial velocity near zero. There it contacts high-velocity inert gas, which is often heated to high temperature to maintain the liquid metal in a fluid state throughout atomization. Initially, relatively large droplets or sheets form, which then undergo secondary atomization by various mechanisms that depend on local flow patterns, flow velocity, mass loading, and the physical properties of the gas and liquid metal.

The dynamics of droplet breakup in high-velocity flows is quite complicated. Historically, the Weber number, *We*, has been a useful predictor of breakup tendency.[3] The parameter *We* represents the ratio of inertial forces to surface tension forces:

$$We = \frac{\rho V^2 D}{2\sigma}$$

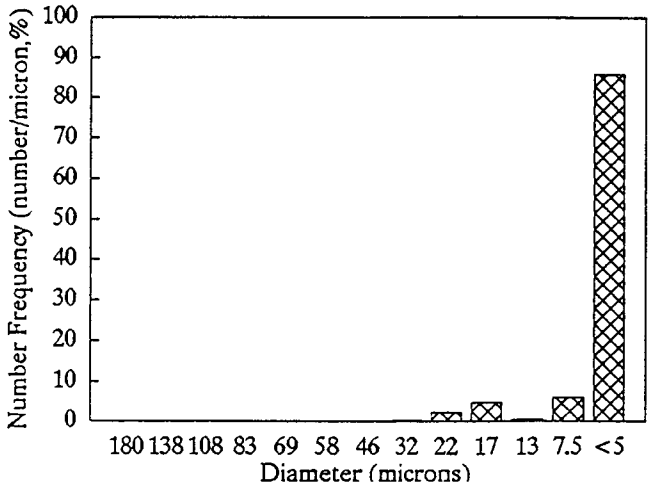


Fig. 3 Number frequency of tin powder.

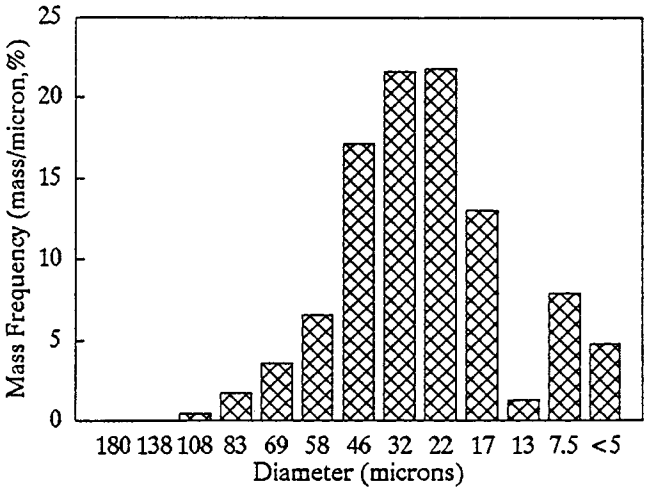


Fig. 4 Mass frequency of tin powder.

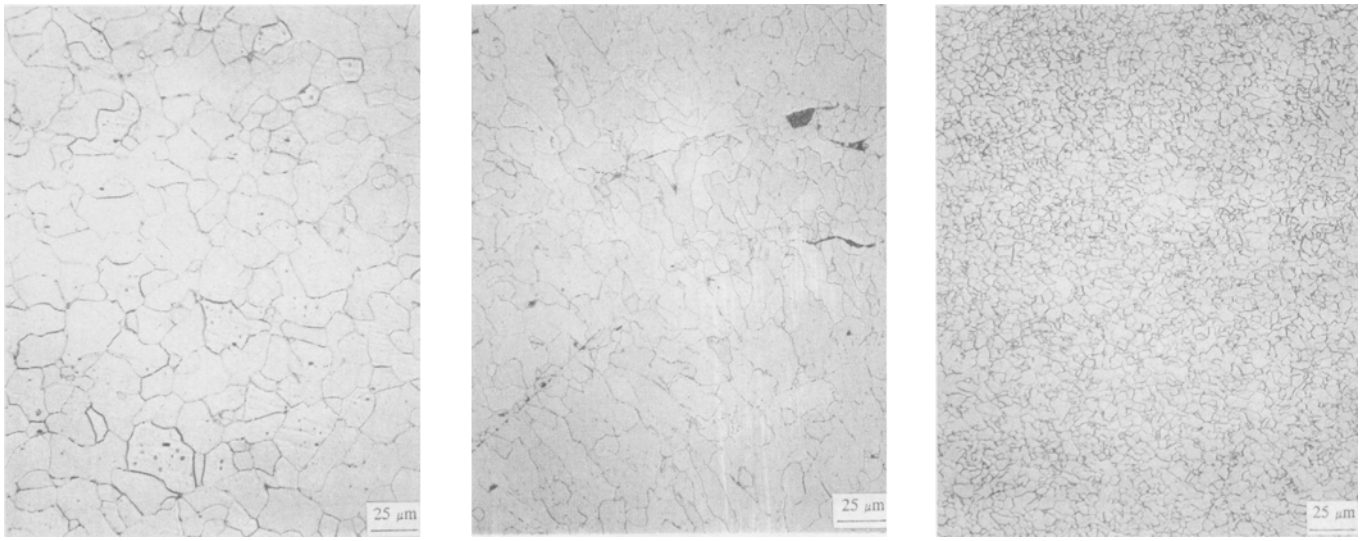
where ρ is the density of the gas; V is the initial relative velocity between the flow field and the drop; D is the initial diameter of the drop; and σ is the surface tension of the drop.[4] Breakup of liquid drops will not occur unless the Weber number exceeds a critical value, We_{crit}. Shock exposure of various liquids has yielded We_{crit} values ranging from about 1 to 25. There are, however, few measured We_{crit} values cited in the literature for liquid metals exposed to high-velocity flows. Haas[5] has observed We_{crit} values between 5 and 6 for mercury drops falling vertically into an opposing high-velocity free jet of air. The critical Weber number associated with the atomization of liquid tin in INEL nozzles is estimated to be close to 1. Atomization occurred using a nozzle operating at an inlet pressure of 207 kPa (30 psia) absolute, with argon gas heated to 300 °C. We_{crit} was calculated for a 14 μm droplet using the surface tension of the bulk liquid at its melting point and the measured gas and droplet flow velocities. The density of the gas was calculated using compressible flow theory. In contrast, the Weber number associated with breakup of a 3-mm tin droplet at the liquid injection point is estimated to be about 280 under the same nozzle conditions.

Atomization usually proceeds through stages, producing a range of droplet sizes. Fincke et al.[6] used high-speed video techniques to examine metal breakup in INEL nozzles and observed at least two breakup mechanisms, depending on the flow conditions and mass loading. One of these, termed "bag breakup," was observed at low nozzle inlet pressures. "Bag breakup" has been observed in a number of studies on a variety of liquids in both steady and transient flow fields. Pilch and Erdman[4] correlated this type of breakup and the related "bag and stamen breakup," with initial Weber numbers $12 < We < 100$. In "bag breakup," the center portion of a drop front surface first becomes concave and then is blown out downstream to form a hollow bag attached to a more massive toroidal rim. The bag bursts, producing a shower of relatively fine droplets and filaments. Surface tension then consolidates the rim into one or more fragments that can also undergo breakup depending upon the Weber number.[3]

Another breakup mechanism, associated with higher initial Weber numbers ($100 < We$), has also been observed in these nozzles. This mechanism, termed "stripping" (e.g., sheet stripping and wave crest stripping), occurs when a droplet deforms in a manner nearly opposite to bag breakup. The drop flattens on the downstream side and presents a convex surface to the flow. Depending on the relative velocity and physical properties of the liquid, the edges of the deformed drop elongate into sheets and fine filaments or drops that later detach.

Examination of unconsolidated powders collected during spray forming with linear de Laval nozzles provides insight into the breakup mechanisms. Normally, an abundance of spherical or near-spherical shapes is found, as the SEM photograph in Fig. 2(a) illustrates. However, other shapes have also been observed. Intermixing of prolate ellipsoidal particles with fine spherical tin particles (Fig. 2b) at moderate flow conditions suggests that the former resulted when liquid tin filaments, generated during bag breakup or stripping, solidified in-flight. Irregular powder shapes (Fig. 2c) were formed at low gas flow rates with the same nozzle. These large, irregular shapes suggest that the parent droplets began to undergo "bulgy" deformation and breakup, as described by Hinze,[7] but were frozen in flight. The bulges and protuberances appear larger than would be expected if they were due solely to solidification shrinkage.

Spray conditions that favor the formation of a narrow droplet size distribution and a small average droplet size are preferred in many spray forming applications. The size distribution of tin powder collected during spray forming experiments was evaluated using wet and dry sieving techniques. The powder was produced using a bench-scale linear de Laval nozzle of the authors' design having a transverse throat width of 17 mm. The nozzle was operated at a pressure of 207 kPa (30 psia) absolute. Argon, heated to about 300 °C, was the atomizing gas. Liquid tin was heated about 70 °C above its melting point and pressure fed into the nozzle through a series of orifices that spanned the width of the nozzle. The gas-to-metal mass flow ratio was measured to be about 10, with a metal throughput of about 31 kg/h. The powder was collected in an argon-purged chamber, passivated with 2% O_2 prior to exposure to the atmosphere, and sieved through fine



(a) (b) (c)

Fig. 5 Microstructure of commercial SAE 1008 hot band, as-deposited, and hot rolled steel. (a) Stock 1008 steel hot band. (b) As-deposited 1008 steel. (c) Hot rolled 1008 steel (1100 °C, 65% thickness reduction).

mesh screens of 300, 250, 210, 150, 125, 90, 75, 63, 53, 38, 25, 18, 15, 10, and 5 μm. Few particles larger than 125 μm were observed.

Figure 3 is a histogram of the count frequency distribution versus powder size. The count frequency is normalized for the sieve size range, expressed as a percentage of the total counts. About 85% of the powder particles were <5 μm in diameter; the average particle size was calculated to be 4 μm. Figure 4 is a histogram that relates mass frequency to powder size for the same sample, again normalized for the size range of the sieves. When compared with Fig. 3, this distribution reflects the significance of the mass weighting factors (which change proportionally as d^3D) imposed by relatively small numbers of more massive particles. Because most spray forming applications are mass intensive, the distribution in Fig. 4 is a more representative description of the powder (and spray plume) size distribution. The Sauter (or area) mean diameter, d_{sm}, and volume mean diameter, d_{vm}, were calculated to be 23 and 31 μm, respectively. The parameter d_{sm} is sensitive to finer droplets, whereas d_{vm} is sensitive to coarser droplets. The mass median diameter, d_m, which corresponds to 50% cumulative weight (d_{50}), was determined to be 23 μm by interpolation of cumulative weight versus size data. The geometric standard deviation, $\sigma_v = (d_{84}/d_{16})^{1/2}$, was calculated to be 1.5, indicating a narrow droplet size distribution in the spray plume.

3. Applications of Spray-Forming Technology with de Laval Nozzles

3.1 *Low-Carbon Steel Strip*

Low-carbon steel strip was spray formed to thicknesses >0.75 mm using a bench-scale spray apparatus described previously.[16] Gas atomization of molten SAE 1008 steel was accomplished using a linear de Laval nozzle of the authors' design. The resultant droplets were entrained in a highly directed two-phase flow and deposited onto a rotating, water-cooled mild steel drum. The spray was directed horizontally; other orientations are possible. The nozzle throat width, transverse to the direction of flow, was about 25 mm. Mass throughputs for this bench-scale nozzle were as high as 1.1 Mg/h (1.2 ton/h) for a slit orifice nozzle operating in the aspiration mode and 4.2 Mg/h (4.6 ton/h) 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 inlet. Single-phase pitot tube flow field measurements indicated that at this driving pressure supersonic (~Mach 1.5) flow conditions existed within the nozzle, with the shock front located in the diverging section near the metal feed location. Gas-to-metal mass flow ratios typically ranged from 0.1 to 0.5. The gas and droplets 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.

During a typical run, 1.5 kg of steel was induction heated to about 100 °C above the liquidus temperature, atomized with argon heated to about 1000 °C, and spray formed into a strip of metal about 127 mm wide and >0.76 mm thick. A transverse cross section of the strip generally exhibited a flat central section with tapered edges. Overspray losses, defined as unconsolidated particulate and thin edge trimmings, could be maintained below 8% for steel and below 4% for tin using bench-scale nozzles. 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 on the sample, hot rolling at 1000 to 1100 °C to 30 to 70% thickness reduction was sufficient. Low porosities

Table 1 Tensile properties of commercial SAE 1008 hot band and spray-formed and hot rolled strip

Sample	Yield strength (0.2% offset), MPa (ksi)	Ultimate strength, MPa (ksi)	Elongation, in 50 mm, %	Vickers hardness (100-g load)
Commercial 1008 hot band	197 (28.6)	306 (44.4)	51.8	91
Spray-formed and hot rolled	290-324 (42.0-47.0)	334-498 (48.4-72.3)	13.9-37.7	136-160

together with fine microstructures were obtained with conditions that favored the formation of dense sprays consisting of small droplets with low solid fractions.

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 from commercial hot band to as-deposited material and finally to hot rolled product is shown in Fig. 5. 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, indicating the heat transfer direction. The grain structure of the spray-formed and hot rolled material was equiaxed ferrite with ~5 μm diameter grains.

Notable improvements in tensile properties resulted from grain structure refinement. Table 1 summarizes the results. The range of values for spray-formed steel reflect differences in spray parameters from run-to-run. Compared to commercial hot band, yield strength and ultimate tensile strength increased as much as 63%. Vickers hardness values were as much as 76% higher, but elongation of the spray-formed and hot rolled material was reduced by about 50%. Elongation values were improved 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.

3.2 *Polymer Membranes*

The transport properties of membranes depend on the membrane microstructure or "fabric," as well as the physicochemical properties of the polymer and the operating conditions.[8] The microstructure, in turn, is influenced by the fabrication method. A study was conducted to examine the feasibility of adapting spray-forming technology to the production of polymer membranes. The results are summarized below.

Membranes of poly[bis(phenoxy)phosphazene] (PPOP) were fabricated by spray forming and by the conventional method, evaporative knife casting. PPOP is an inorganic polymer material with exceptional stability in the adverse thermal (>100 °C) and chemical (high or low pH extremes) environments frequently encountered in industrial separations.[9] The ability of the membranes to separate components of several gas mixtures was compared.

Spray-formed membranes were produced by depositing atomized droplets of linear PPOP dissolved in tetrahydrofuran (THF) onto glass substrates. 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. The solution was warmed to ~45 °C to lower its viscosity and was poured into the tundish of the nozzle, which operated at a static pressure of 137 kPa (20 psia). The solution was aspirated into the nozzle through six small orifices. Solution throughput was about 0.4 kg/s per meter of nozzle throat width. The corresponding gas-to-polymer solution mass flow ratio was about 4. Solvent molecules were shed from the atomized droplets during their flight, and the remainder evaporated at the substrate. Although 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. A typical membrane measuring 83 m × 83 mm × 5 μm thick was fully consolidated and dried in about 1 s.

Gas chromatography was used to evaluate the selectivity (i.e., the permeability ratio of the components) of spray-formed and knife cast PPOP membranes for several acid gas mixtures (10% SO_2/90% N_2, 10% H_2S/90% CH_4, 10% CO_2/90% CH_4). At 80 °C, spray-formed membranes had four times the selectivity of knife cast membranes when separating SO_2 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 H_2S from methane at 80 °C and had 67 times the selectivity at 130 °C. Improvements were also observed with spray-formed membranes when separating CO_2/CH_4 mixtures.

Membrane fabrication via spray forming was found to offer time savings, flexibility, and improved performance over traditional approaches (e.g., knife or spin casting). Whereas knife cast membrane preparation required hours, spray-formed membranes were prepared in seconds. 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.

4. Conclusions

The atomization of liquid metals in linear de Laval spray forming nozzles was briefly described. These nozzles can provide highly directed sprays of fine metal or polymer droplets with a narrow distribution of droplet size. The ability to do so over a wide range of liquid flow rates makes these nozzles useful in a number of spray forming applications. This was exemplified using two extreme cases—the high volume/high tonnage production of low-carbon steel strip and the production of delicate polymer membranes for use in chemical separations.

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