EGG-M-92421
CONF-9202168--1

EGG-M--92421

DE93 010793

RECENT INEL SPRAY-FORMING DEVELOPMENTS

Kevin M. McHugh and James F. Key
Idaho National Engineering Laboratory
Idaho Falls, ID 83415-2050

ABSTRACT

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, oftentimes while 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 using de Laval nozzles. Results from several spray-forming programs are presented to illustrate the range of capabilities of the approach as well as the technical and economic benefits. These programs involved the production of low-carbon steel strip and SiC particulate reinforced aluminum strip; recent advances in spray forming tooling using low-melting-point metals are also described.

INTRODUCTION

Researchers at the INEL are developing spray forming technology using linear de Laval (converging/diverging) nozzle designs to produce solids and coatings of a variety of materials. The approach combines unique spray nozzle designs with on-line diagnostics of the spray plume and product quality. 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. Guidance for component design and process control is provided by modeling efforts in multiphase flow, heat transfer, and solidification phenomena.

During operation, the spray nozzle generates a low static pressure region near the nozzle's throat. Metals, polymers, and composite materials have been spray formed by aspirating or pressure feeding the liquid through a slit orifice or a series of circular orifices that span the width of the nozzle. A high-velocity, high-temperature inert gas atomizes the liquid; the resultant droplets are entrained by the gas stream and deposited onto a substrate. In-flight convection cooling of the droplets followed by conduction and convection cooling at the substrate result 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. Figure 1 illustrates the rapid solidification and near-net-shape qualities of this approach. The semispherical shell was generated by spray depositing molten tin directly onto an inflated party balloon.

LOW-CARBON STEEL STRIP

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; low cooling rates result in coarse, dendritic microstructures. The material must be 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 the strip and further refines the metal's microstructure. This can lead to enormous cost savings. A 1990 technoeconomic analysis compared operating costs for producing low-carbon steel hot band, the industry's highest volume commodity, by spray forming, continuous casting, and thin slab casting [1]. Cost improvements using spray forming were about 50% compared to continuous cast steel, and 18% compared to thin slab casting. These savings are due primarily to elimination of unit operations and associated energy costs. Improvements in product quality can be equally impressive. For example, after hot rolling to ~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.

The INEL spray-forming approach for producing continuous metal strip is depicted schematically in Figure 2. Gas atomization of a molten metal feedstock is accomplished using a converging-diverging (de Laval) nozzle; the resultant droplets are entrained in a highly directed two-phase flow and deposited onto a rotating, water-cooled drum. Rapid solidification of the deposit restricts grain growth and improves product homogeneity by reducing the segregation of impurities that form inclusions.

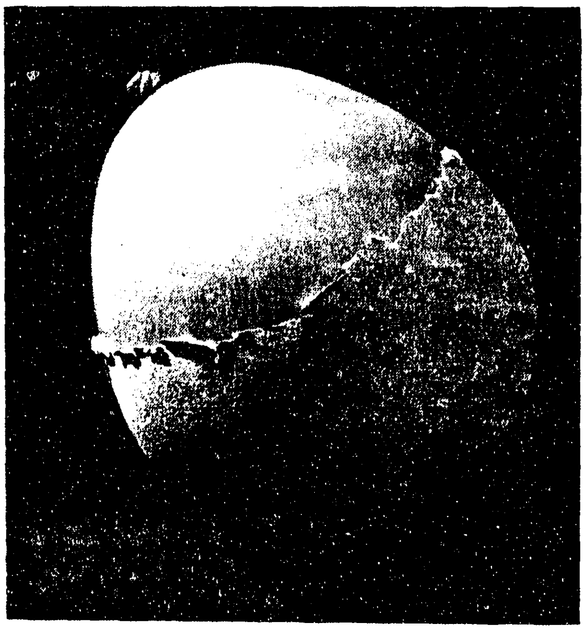

Figure 1. Party balloon spray coated with tin demonstrates rapid solidification and near-net-shape forming capability of spray forming.

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 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. A purged argon atmosphere within the spray system minimized slag formation in the melt, surface oxidation of the strip, and in-flight oxidation of the atomized droplets.

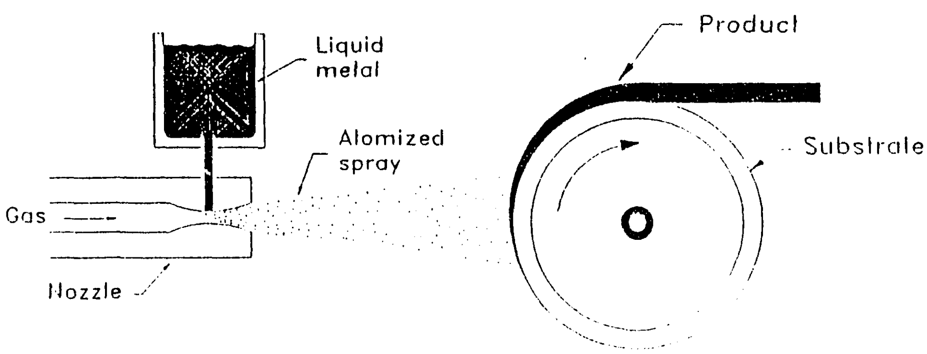

Figure 2. Schematic of approach for spray forming metal strip.

Bench-scale linear converging/diverging nozzles of our own design were machined in-house from boron nitride and composites of BN with AlN. Boron nitride was chosen due to its refractory properties and excellent machinability. Interchangeable inserts of high purity Al_2O_3 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. This throughput seemed to be a practical limit when aspirating liquid steel into the nozzle's flow channel at only one location due to localized gas flow perturbations which reduce the suction. Higher throughputs are possible by aspirating liquid steel into the nozzle at multiple locations. Mass throughputs were measured to be 165 Mg/h•m for the same nozzle operating in the pressurized feed mode.

The gas flow field was mapped under single-phase flow conditions using small pitot tube probes. A typical nozzle inlet pressure of 206 kPa (30 psia) absolute was found to generate supersonic flow conditions with the shock front located 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 droplets cooled rapidly after exiting the nozzle as the spray plume entrained cool ambient argon. Gas and droplet velocity decreased after exiting the nozzle, with large droplets responding less to drag effects by virtue of their greater momentum.

The sprayed 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. Overspray losses, defined as unconsolidated droplets and thin edge trimmings, could be maintained below 8% for steel, and below 4% for tin using bench-scale nozzles.

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 3. 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 grains.

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 (10^4 to 10^8°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 4. 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.

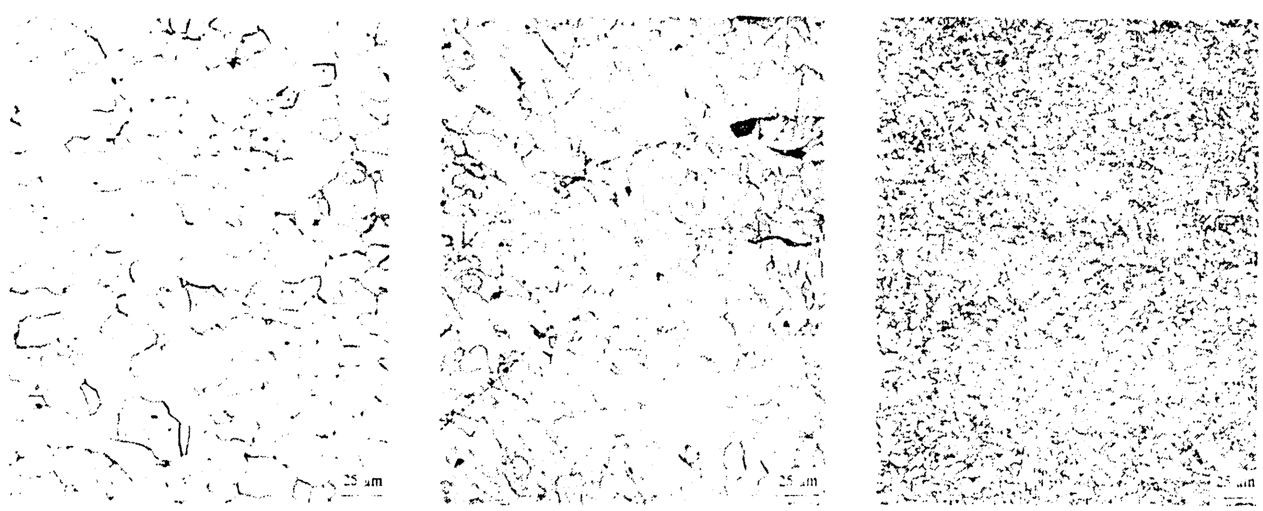

Figure 3. Microstructure (left to right) of commercial SAE 1008 hot band, as-deposited, and hot-rolled steel.

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 in processing parameters, particularly spraying conditions, for different spray trials. 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.

PARTICULATE REINFORCED METAL MATRIX COMPOSITES

Metal matrix composites (MMCs) combine metallic properties such as high thermal and electrical conductivity, toughness, and thermal shock resistance with ceramic properties such as corrosion resistance, strength, high modulus, and wear resistance [7-16]. The partitioning of these properties depends on the choice and volume fraction of ceramic and metal, but usually the improved properties come at some cost, such as loss of ductility and toughness relative to the matrix material [17]. A variety of casting and powder metallurgical processing methods for particulate reinforced metal matrix composites have become available over the last two decades and these efforts have spawned several commercial products. The development of efficient processing technologies, however, remains the greatest roadblock to large-scale commercial use of particulate reinforced metal matrix composites. In a recent workshop sponsored by the Office of Naval Research, processing was found to be the most important area for current research and development of MMCs [18,19]. Innovative development was found to be urgently needed in near-net-shape production technologies, in particular in semifinished shapes (rods, tubes, and strip).

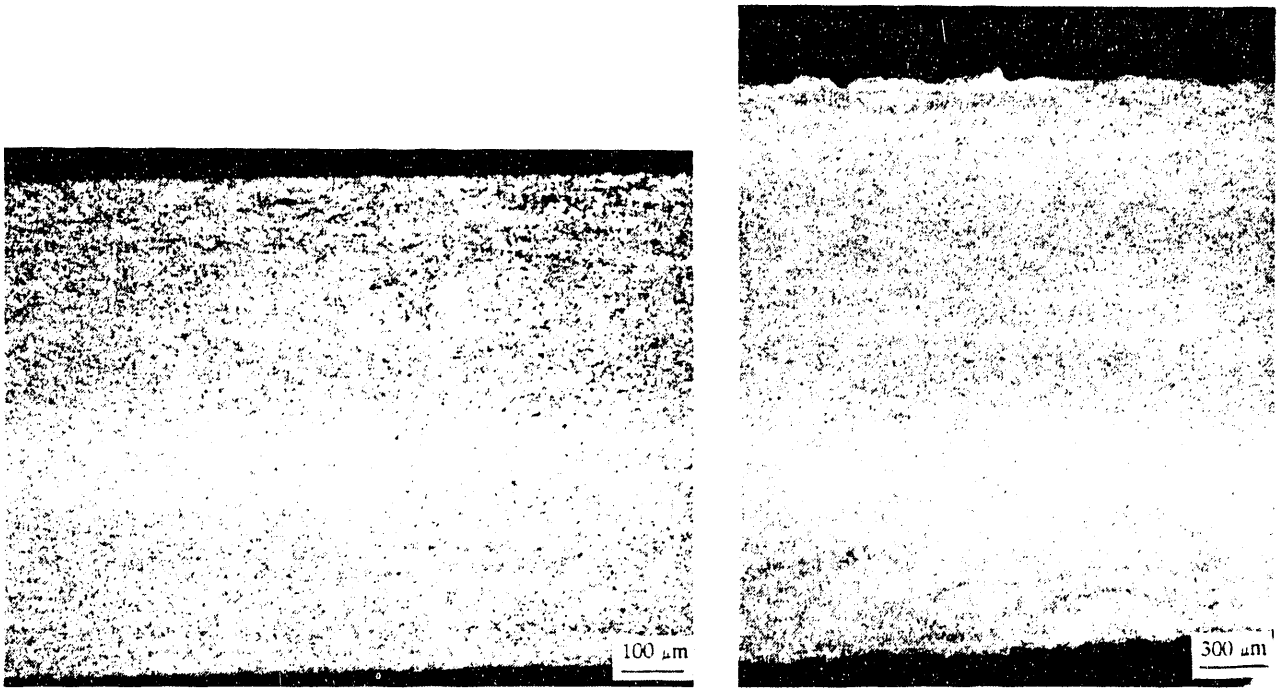

Figure 4. Microstructure of thin, spray-formed and hot-rolled strip.

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

Sample	Yield Strength, 0.2% Offset, MPa (ksi)	Ultimate Strength, MPa (ksi)	Elongation in 50 mm, %	Hardness, DPH, 100 g Loads
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

Spray forming is a unique processing approach for particulate reinforced MMCs that offers flexibility and control of particulate volume fraction together with inherent near-net-shape and rapid solidification fabrication capabilities. Process flexibility and a reduction in the number of unit operations translates to substantial savings in time, capital equipment, and energy. The INEL approach for spray forming particulate reinforced metal matrix composites in continuous strip form is similar to that depicted in Figure 2. The reinforcement phase is pressure fed into the nozzle in the form of an aerosol upstream of the entry location of the molten metal. The particulate enters the nozzle at or near room temperature, but is quickly heated by the atomizing gas to the desired temperature. The liquid metal is heated about 100°C above its liquidus temperature, pressure fed into the nozzle, atomized, and codeposited with the reinforcement phase. Gas and liquid metal temperature control allow control of the extent of matrix/particulate wetting and interfacial reactions. The transit time of the multiphase flow to the substrate is on the order of milliseconds. Upon impacting the substrate, matrix solidification rates are expected to be high ($>10^3$ K/s), significantly restricting the macrosegregation effects often observed in slowly-cooled cast composites [20]. This approach, therefore, largely bypasses two major problem areas in most particulate reinforced MMC fabrication methods--control of matrix/particulate interfacial reactions and wetting, and nonuniform blending caused by density differences between the matrix and reinforcement phases [21-24].
Composite strip of 6061 aluminum reinforced with SiC particulate (~13 μm diameter) was spray formed. Particulate volume fraction ranged from 4 to 15%, as determined by acid dissolution of the matrix. Optical microscopy of polished samples indicated a uniform distribution of particulate in the matrix phase; an example is given in Figure 5. As-deposited density of the matrix strip, measured by water displacement using Archimedes' principle, was 90 to 95% of theoretical. Photomicrographs of polished samples, however, revealed that as little as 30% thickness reduction was needed for full densification.

As-deposited composite strip was sectioned and hot rolled at 450°C to 80% thickness reduction. Samples were then heat treated to yield a -T6 temper. Room temperature tensile properties were evaluated for eight samples. The composite material had small but significant (about 10%) improvements in ultimate and yield strength over commercial 6061-T6 strip, but a reduction in elongation. Ultimate tensile strength, yield strength, and elongation were as high as 337 MPa, 308 MPa, and 9.5% respectively, in the spray formed and hot-rolled composite strip. The tensile strength of commercial 6061-T6 aluminum strip is typically about 310 MPa, with a yield strength of 275 MPa and an elongation of 12% [25]. While these preliminary results are encouraging, evaluation of a larger number of samples is necessary to establish statistical validity.

Figure 5. Photomicrograph of unetched rolled composite strip showing distribution of SiC particulate in Al-6061 matrix.

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 [26], stereolithography [27], 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 [28]. Methodologies that can rapidly produce specialized tooling, such as molds and dies, when used with conventional approaches such as injection molding, compression molding, and die casting, would satisfy this goal.

Presently, making complex molds, dies, and related tooling is expensive and time consuming. They can exceed $200K in cost and require months to fabricate. Researchers at INEL have recently begun to develop technology to produce specialized tooling by spray depositing molten metal droplets onto patterns made from plastics, waxes, clay, and 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.

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) 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.

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 also was very good. Patterns of a variety of other plastics, including acrylic, polycarbonate, and polystyrene, have also given good results.

Figure 6. Metal mold shell (left) was produced in about 5 min by spray depositing tin onto plastic pattern (right).

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. Figure 8 is a histogram that gives the count frequency vs. powder size. The ordinate gives the count frequency normalized for the sieve size range, expressed as a percentage of the total counts. The plot indicates that about 85% of the powder particles were <5 μm in diameter. The average particle size was calculated to be 4 μm. The histogram in Figure 9 relates mass frequency to powder size for the same tin powder sample, again normalized for the size range of the sieves. When compared with Figure 8, this distribution reflects the significance of the mass weighting factors (which go as d^3) imposed by relatively small numbers of more mas-sive particles. Since most spray-forming applications are mass intensive, the distribution in Figure 9 is a more representative description of the powder (and spray plume) size distribution. The Sauter (or area) mean diameter,

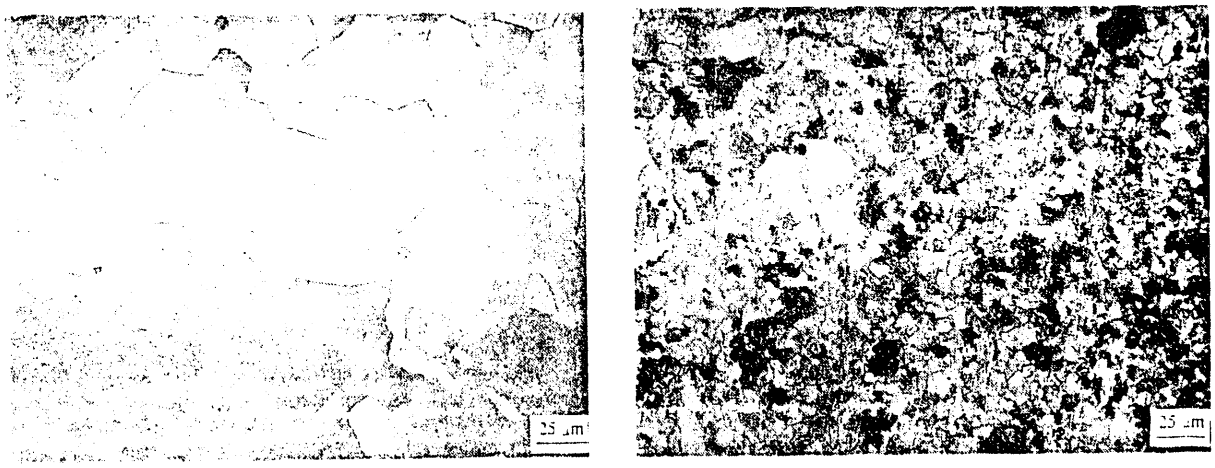

Figure 7. Microstructures of cast tin (left) and spray-formed tin mold of Figure 6 (right).

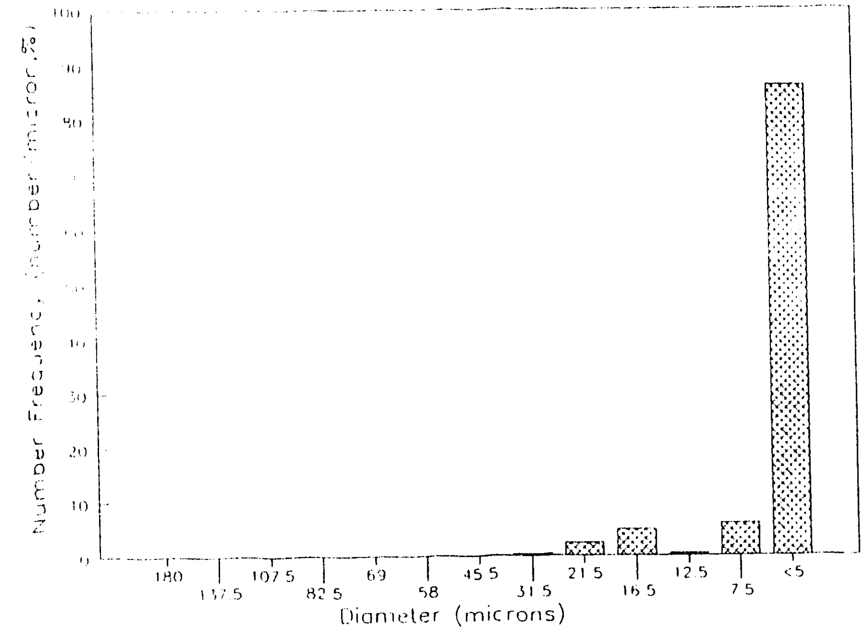

Figure 8. Number frequency of tin powder.

d_{sm}, and volume mean diameter, d_{vm}, were calculated to be 23 and 31 μm, respectively. d_{sm} is particularly useful in evaluating droplet sizes for surface area intensive processes such as combustion of fuels and spray drying. It is sensitive to finer droplets while d_{vm} is sensitive to coarser droplets. Together they give a balanced view of the powder size. The mass median diameter, d_m, was determined to be 23 μm by interpolation of the cumulative weight vs. size data. It is the diameter corresponding to 50% cumulative weight (d_{50}). 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. 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 from Ray Berry in modeling multiphase flow behavior, heat transfer, and solidification phenomena; Denis Clark in substrate development, process control, and modeling efforts in spray deposition; and James Fincke and David Swank in particle and gas flow field diagnostics. 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.

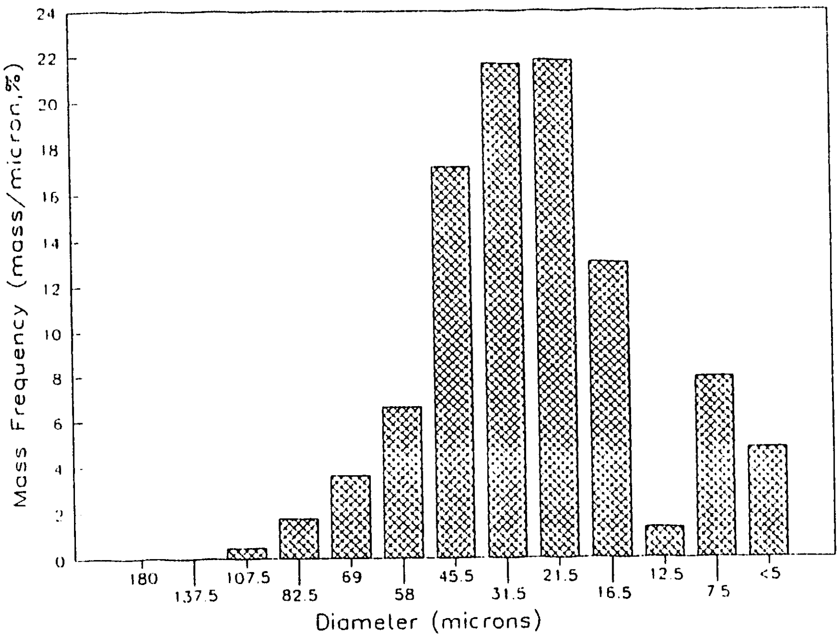

Figure 9. Mass frequency of tin powder.

REFERENCES

1. W. DuBroff, Private Communication, 1992.
2. J. F. Key, R. A. Berry, D. E. Clark, J. R. Fincke, and K. M. McHugh, *Development of a Spray-Forming Process for Steel. Final Program Report*, Dec. 1991.
3. A. R. E. Singer, *Powder Metal.* **25** (4), 195 (1982).
4. P. Predecki, A. W. Mullendore, and N. J. Grant, *Trans. Metall. Soc. AIME* **233**, 1581 (1965).
5. P. Duwez and R. H. Willens, *Trans. Metall. Soc. AIME* **227**, 362 (1963).
6. R. C. Ruhl, *Mater. Sci. Eng.* **1**, 313 (1967).
7. A. L. Geiger and J. Andrew Walker, *JOM*, August 1991, p. 8.
8. M. Paley and J. Aboudi, *Composites Science and Technology* **41**, 411 (1991).
9. A. P. Divecha, S. G. Fishman and S. D. Karmarker, *JOM*, Sept. 1981, p. 12.
10. A. P. Divecha and S. G. Fishman, *Proceedings of the 3rd International Conference on the Mechanical Behavior of Materials*, K. J. Miller and R. F. Smith, eds., Pergamon Press, New York, NY, 1980, p. 351.
11. V. C. Nordone, J. R. Strife and K. M. Prewo, *Metall. Trans.* **22A**, 171 (1991).
12. S. V. Nair, J. K. Tien and R. C. Bates, *Int. Metals Rev.* **30**, 275 (1985).
13. V. C. Nardone, *Scripta Metall.* **21**, 1313 (1987).
14. T. G. Nieh, *Metall. Trans.* **15A**, 139 (1984).
15. Y. Wu and E. J. Lavernia, *JOM*, August 1991, p. 16.
16. I. A. Ibrahim, F. A. Mohamed, and E. J. Lavernia, *J. Mat. Sci.* **26**, 1137 (1991).
17. F. A. Girot, T. M. Quenisset and R. Naslan, *Composite Sci. Technol.* **30**, 155 (1987).
18. *Critical Research Directions in Metal-Matrix Composites.* ESNIB 91-03, p. 18.
19. *The Materials Revolution through the 90's - Powders, Metal Matrix Composites, and Magnetics*, ESNIB 89-10, p. 4.
20. S. K. Das and L. A. Davis, *Mater. Sci. Eng.* **98**, 1 (1988).
21. N. Zhang and Y. Wang, *Vacuum* **42** (15), 1017 (1991).
22. R. C. Pond, *Grain Boundary Structure and Kinetics*, ASM, Metals Park, Ohio, 1980, p. 13.
23. O. L. Krivanek, S. Isoda and K. Kobayashi, *Phil. Mag.* **36**, 931 (1977).
24. W. Krakow and D. A. Smith, *J. Mater. Res.* 1, 47 (1986).
25. *Metals Handbook Desk Edition*, eds., H. E. Boyer and T. L. Gall, ASM, Metals Park, OH, 1989, p. 6.35.
26. C. R. Deckard, *Manufacturing Processes, Systems, and Machines: 14th Conference on Production Research and Technology*, S. K. Samanta, Ed., NSF, Ann Arbor, MI, 1987.
27. L. E. Weiss, E. L. Gursoz, F. B. Prinz, P. S. Fussell, S. Mahalingam, and F. P. Patrick, *Manufacturing Review* 3 (1), 40 (1990).
28. S. Ashley, *Mechanical Engineering*, **113** (4), 34 (1991).

END

DATE FILMED

6/22/93