

NEAR-NET-SHAPE MANUFACTURING:
SPRAY-FORMED METAL MATRIX COMPOSITES AND TOOLING

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ABSTRACT

Spray forming is a materials processing technology in which a bulk liquid metal is converted to a spray of fine droplets and deposited onto a substrate or pattern to form a near-net-shape 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. The Idaho National Engineering Laboratory is developing a unique spray-forming method, the Controlled Aspiration Process (CAP), to produce near-net-shape solids and coatings of metals, polymers, and composite materials. Results from two spray-forming programs are presented to illustrate the range of capabilities of the CAP approach as well as the accompanying technical and economic benefits. These programs involved spray forming aluminum strip reinforced with SiC particulate, and the production of tooling, such as injection molds and dies, using low-melting-point metals.

INTRODUCTION

In spray forming, liquid metal is converted to a spray of fine droplets and deposited onto a substrate or pattern to form a near-net-shape solid. Researchers at the Idaho National Engineering Laboratory are developing a unique spray-forming method, the Controlled Aspiration Process (CAP), to produce near-net-shape deposits of metals, polymers, metal matrix composites, and polymer matrix composites. CAP differs in design, operation, and performance from conventional spray forming. 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 resulting shower of droplets impinges upon a moving substrate to form a solid deposit. In contrast, CAP uses a close-coupled atomization technique in which 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 fine droplets and entrains the droplets in a highly directed spray that can have any orientation.

Spray deposition with CAP nozzles typically involves transonic gas-particle flow through the nozzle and subsonic free jet flow from the nozzle to the substrate. After exiting the nozzle, metal droplets undergo rapid in-flight cooling, due to convection heat transfer to the surrounding inert gas, becoming partially solidified and undercooled. Upon impacting the substrate, the droplets weld together to form a coherent solid while releasing the remaining enthalpy by convection and conduction through the substrate. The unusually high cooling rates (normally $> 10^3$ K/s) result in a rapidly solidified product that can offer property improvements such as refined microstructures, extended solid solubilities, and reduced segregation compared to cast materials. The process provides economic advantages because the product is near-net-shape and fewer unit operations, such as machining, forging, or rolling, are required.

CAP is very versatile. Metals have been spray formed by feeding the melt through a slit orifice or a series of circular orifices that span the width of the nozzle. Polymers are dissolved in an appropriate solvent before spraying or, in some cases, a melt or plasticized melt is sprayed. Metal matrix composites, polymer matrix composites, and unique alloy systems are produced by codeposition of the phases.

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). Toward that end, an in-flight particle diagnostics system is used to simultaneously measure droplet size, velocity, and temperature in the atomized plume. This system measures particle diameters between 5 and 1,000 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; particle temperature is measured with a high-speed two-color pyrometry technique. Modeling the multiphase flow, heat transfer, and solidification phenomena provides guidance for component design and process control.

While the nozzle design and operating parameters are customized for a particular application, 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. Applications include strip and sheet products, cylindrical and tubular products, tooling such as molds and dies, near-net-shape structural products, rapidly-solidified metal alloy products, superplastic alloy products, metal matrix composites, controlled porosity materials for membranes and electrodes, metal claddings, coatings for metals and nonmetals, and polymer products.

Results from two spray-forming programs are presented to illustrate the range of capabilities of CAP as well as the accompanying technical and economic benefits. These programs involved spray-forming aluminum strip reinforced with SiC particulate, and the production of tooling, such as injection molds and dies, using low-melting-point metals.

PARTICULATE-REINFORCED METAL MATRIX COMPOSITES

Metal matrix composites (MMCs) combine the properties of metals, 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 [1-10]. The composite's properties reflect a partitioning of the properties of the ceramic and metal based on the chemical nature and volume fraction of the components. However, improvements in certain properties usually come at some cost, such as a decrease in ductility and toughness relative to the matrix material [11]. Although the ability to tailor the properties of these "materials by design" makes them attractive candidates to the automotive, aerospace, and other industries for a variety of applications, lack of efficient processing technologies is a great impediment to large-scale commercial use of particulate-reinforced MMCs. Recent workshops devoted to evaluating priorities for future MMC research and development have concluded that processing is the most critical area for R&D, particularly near-net-shape production technologies for widely used shapes such as rods, tubes, and strip [12,13].

A variety of processing methods for particulate-reinforced MMCs have been devised over the last two decades. Casting techniques such as squeeze casting [14,15], melt oxidation processing [16,17], melt infiltration processing [18-20], and rheocasting [21] have received the greatest attention and have spawned several commercial products such as the Toyota diesel piston [10,22]. Susceptibility to interfacial reactions, segregation by gravity, particle agglomeration, segregation of the secondary phases in the metal matrix, and coarse matrix grain size have limited the scope of these techniques [10,23].

Powder metallurgical processing circumvents the problems associated with mixing and low cooling rate by cold mixing the components in powder form, followed by compressing, degassing, and final consolidation by extrusion, forging, rolling or other hot working below the liquidus of the matrix [10,24]. While this technique generates products with better properties, and is usually more reliable, than the casting routes, it is also more costly [25]. The rapidly-solidified matrix powders normally used are relatively expensive starting materials, and pressing equipment places limitations on component size. Furthermore, while interfacial reactions are reduced, poor particulate wetting by the matrix material has often led to the use of precoated particulate, another increased expense.

Spray forming is a unique processing method for particulate reinforced MMCs that combines rapid solidification processing and near-net-shape fabrication into a single step. By so doing, it simplifies processing, relative to powder metallurgy techniques, while bypassing difficulties found with most casting

methods--matrix/particulate interfacial reactions and nonuniform blending caused by density differences between the matrix and reinforcement phases [26-31]. The high rate of solidification inherent to the process improves the matrix properties and also enables the use of alloys prone to segregation. This extends the range of applications to include competitively-priced composites in which the matrix phase is in a metastable state.

Strip Preparation and Properties

CAP was used to produce composite strip of 6061 aluminum alloy reinforced with SiC particulate. The approach, illustrated schematically in Figure 1, involved codeposition of the phases onto a water-cooled, grit-blasted, mild steel drum. The ceramic phase was pressure-fed into the nozzle in the form of an aerosol upstream of the molten metal, which was also pressure-fed into the nozzle. Heat transfer from the atomizing gas was used to adjust the temperature of the ceramic particulate as it accelerated through the nozzle to the liquid metal atomization region. This approach provided independent control of the feed rates of the liquid metal and ceramic, good component mixing, and independent control of the temperatures of the metal and ceramic inside the nozzle.

Figure 2 shows the temperature response of the atomizing gas (argon) and particulate ($1\ \mu\text{m}$ SiC) as they travel through the nozzle from the inlet to the exit. The gas temperature is approximately constant until the gas accelerates as it approaches the nozzle's throat. The dramatic cooling effect is abruptly terminated at the location of the shock front, which, in this example, is located inside the nozzle. The particulate entered the nozzle at room temperature, but was quickly heated by the atomizing gas. The thermal profile of the particulate is similar to that of the gas except that it responds more sluggishly due to its greater thermal inertia. Figure 3 is a plot of the temperature of the SiC particulate at the location of molten 6061 Al injection into the nozzle. It further illustrates the degree of control of particulate temperature that is gained using CAP.

The spray-forming apparatus used for continuous strip production has been described previously [32]. The modular design 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 a 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. The in-flight particle diagnostics system is used to simultaneously measure single particle size, velocity, and temperature in the atomized plume.

A custom-designed, bench-scale linear converging/diverging spray nozzle was machined in-house from boron nitride with a throat width, transverse to the direction of flow, of about 17 mm (0.66 in.). The

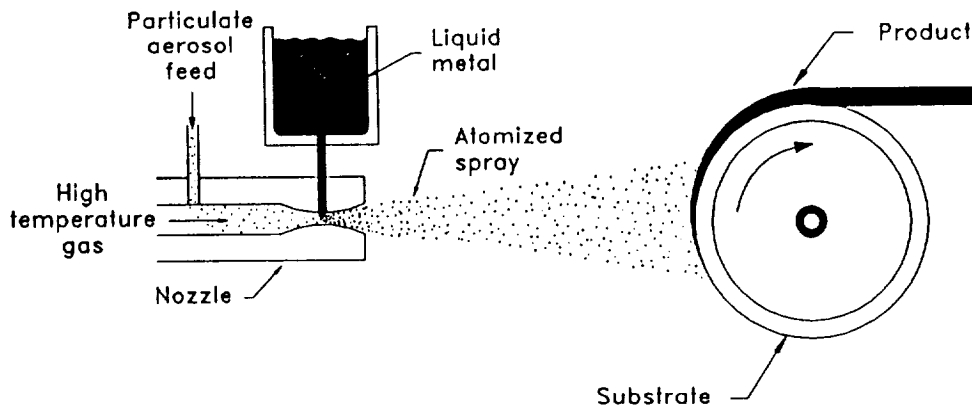


Fig. 1. Schematic of spray-forming composite strip.

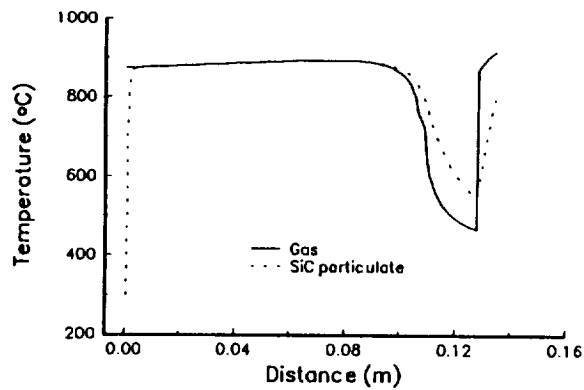


Fig. 2. Temperature profile of atomizing gas and particulate inside nozzle.

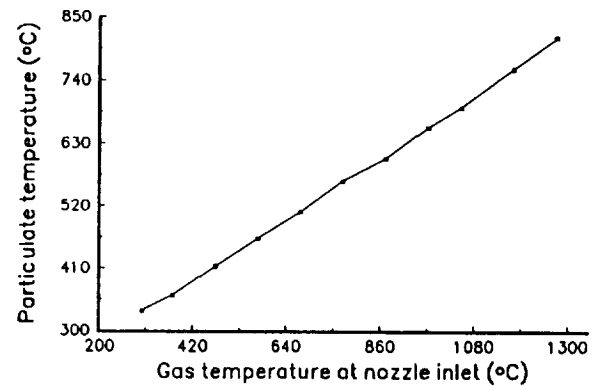


Fig. 3. Particulate temperature at liquid metal injection location as a function of gas temperature at nozzle inlet.

nozzle operates at a static pressure of 206 kPa (30 psia) absolute, measured at the inlet. Single-phase flow field measurements with pitot tubes indicated that this pressure gives rise to supersonic conditions inside the nozzle with the shock front located near the inlet of the liquid metal.

During a typical run, 0.5 kg of 6061 aluminum alloy was induction heated to about 150°C above the liquidus temperature and atomized with argon heated to about 750°C. A commercial fluidized bed powder feed device was used to introduce 13 μm diameter SiC particulate into the nozzle in aerosol form. After a transit time on the order of milliseconds, the multiphase flow impacted the substrate, positioned about 0.3 m from the nozzle, producing a strip of metal about 13 mm (0.5 in.) thick. A purged argon atmosphere within the spray apparatus minimized oxidation of the melt, surface oxidation of the strip, and in-flight oxidation of the atomized droplets.

Aluminum throughput was as high as 700 kg/h (0.8 ton/h), with a corresponding gas-to-metal mass flow ratio (G/M) of 0.1. G/M values as high as 7 were found to give acceptable results. The as-deposited density of the Al strip (without reinforcement), measured by water displacement using Archimedes' principle, was 90 to 95% of theoretical. Photomicrographs of polished strip samples taken at 10% increments in thickness reduction revealed that as little as 30% thickness reduction was needed for full densification (Figure 4).

As-deposited composite strip was sectioned, heated to 450°C in an argon-purged furnace, and hot rolled to 80% thickness reduction followed by quenching. Samples were then solution heat treated and precipitation hardened to yield a -T6 temper. Depending on spray conditions, 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.

Room temperature tensile properties were determined for spray-formed and hot-rolled matrix and 4 vol% composite samples; these results are summarized in Table 1. Both materials showed improvements (about 10%) in ultimate strength and yield strength over commercial 6061-T6 strip, but a reduction in elongation. The unreinforced spray-formed and hot-rolled material also had about 10% higher elastic modulus than commercial 6061-T6. The composite material exhibited a notable increase in modulus (about 33%).

These results are very encouraging but should be viewed as preliminary. Evaluation of a larger number of samples is necessary to optimize spray conditions and to establish statistical validity.

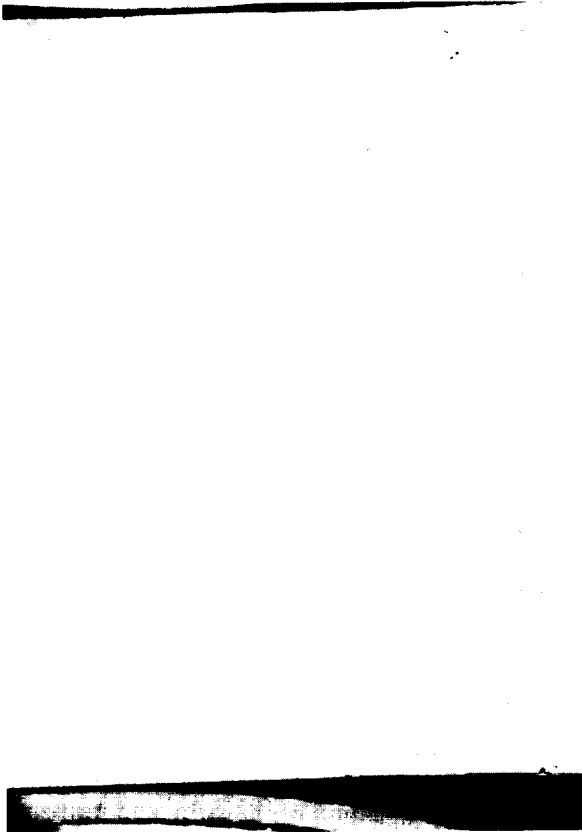


Fig. 4. Photomicrograph of polished matrix strip hot rolled to 30% reduction in thickness.

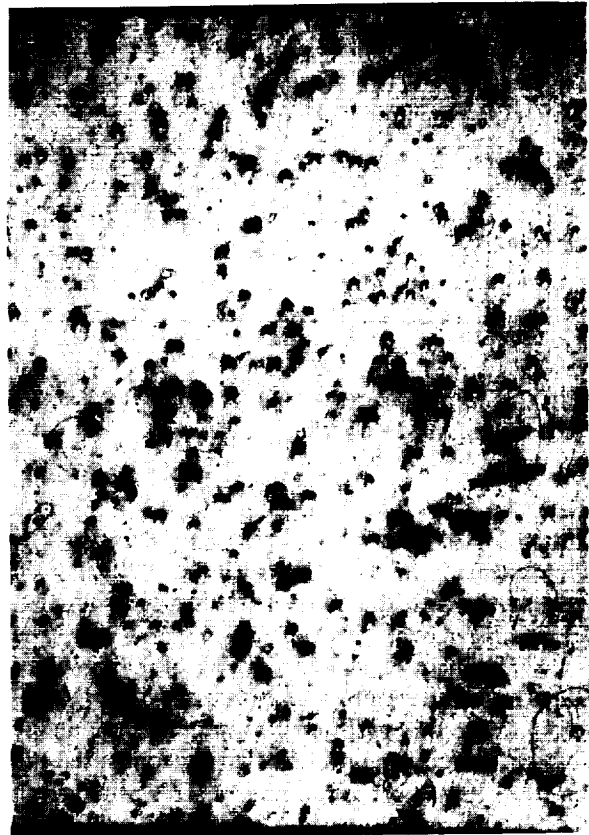


Fig. 5. Photomicrograph of hot rolled 15 vol% 6061/SiC_p composite strip. Polished, unetched.

Table 1. Tensile Properties of 6061 Al and 6061 Al/SiC_p Strip.

Sample	Yield Strength, 0.2% Offset, MPa (ksi)	Ultimate Strength, MPa (ksi)	Elongation in 50 mm, %	Elastic Modulus, GPa
Commercial 6061-T6	277.2 (40.2)	307.5 (44.6)	12.1	70
Spray Formed and Hot Rolled* 6061-T6	306.1 (44.4)	320.6 (46.5)	7.4	77
Spray Formed and Hot Rolled* 6061-T6/SiC _p (4 vol %)	307.5 (44.6)	336.5 (48.8)	5.4	93

*80% thickness reduction

SPRAY-FORMED TOOLING

Interest in rapid prototyping is growing because successful competition in global markets requires the ability to carry a design from its conception through the prototype stage to the production stage faster and at lower cost than ever before. The main long-term goal of rapid prototyping is quick, cost-effective production of prototype parts from the engineered materials that will actually see service.

Specialized tooling, such as injection molds and stamping dies, is used to produce prototype parts and, eventually, production parts. However, this tooling is both costly and time consuming to make. Most specialized tools, even for low-volume production runs, cost about \$20K to \$200K and can require months to fabricate. Large stamping dies can exceed \$1M. As a result, only the most conservative ideas ever reach the showroom or marketplace.

Researchers at INEL are developing spray-forming methods, based on CAP, to produce tooling by spray depositing rapidly quenched molten metal droplets onto patterns of plastic, wax, wood, clay, and other easy-to-form materials. The approach, which combines rapid solidification processing with near-net-shape fabrication, significantly simplifies the production of complex tooling, thereby reducing its cost and production time. Rapid solidification enables patterns made from plastic, wax, clay, etc. to be used for many applications despite their low softening temperatures, while near-net-shape fabrication allows objects with complex shapes to be made easily. The CAP method is compatible with most pattern making methods, including solid freeform fabrication techniques such as selective laser sintering, stereolithography, laminated object manufacturing, solid ground curing, and fused deposition modeling. These methods share the ability to build up 3-D models of prototype plastic or wax, directly from CAD drawings, in a sequential, step-like fashion [33-35].

Approach

CAP was adapted to spray form molds and dies. Nozzle designs and operating conditions that favored the formation of finely atomized droplets having a narrow size distribution were used. These conditions offer the greatest flexibility for controlling droplet temperature and liquid fraction, the flow pattern and momentum of the spray, and, consequently, the microstructure of the deposit. A quasi one-dimensional computer model was used to estimate droplet temperature and solid fraction as a function of spray parameters. 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.

All the spray system components were designed and constructed in-house. The main spray-forming components (spray nozzle, liquid metal reservoir, gas heater, and pattern) were enclosed in an inert-gas-purged glove box to limit the detrimental effects of oxide formation. Bench-scale nozzles having transverse throat widths of 17 mm (0.66 in.) were operated at gas-to-metal mass flow ratios as high as 10. Typically, the metal throughput was about 7 kg/h (15 lb/h) during the initial deposition stage as the pattern's surface features were replicated. Throughput was then increased to about 45 kg/h (100 lb/h) until the walls of the mold were the desired thickness. Much higher deposition rates are possible. A variety of commercial 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). Argon, nitrogen, and helium have been used as atomizing and purge gases with comparable results.

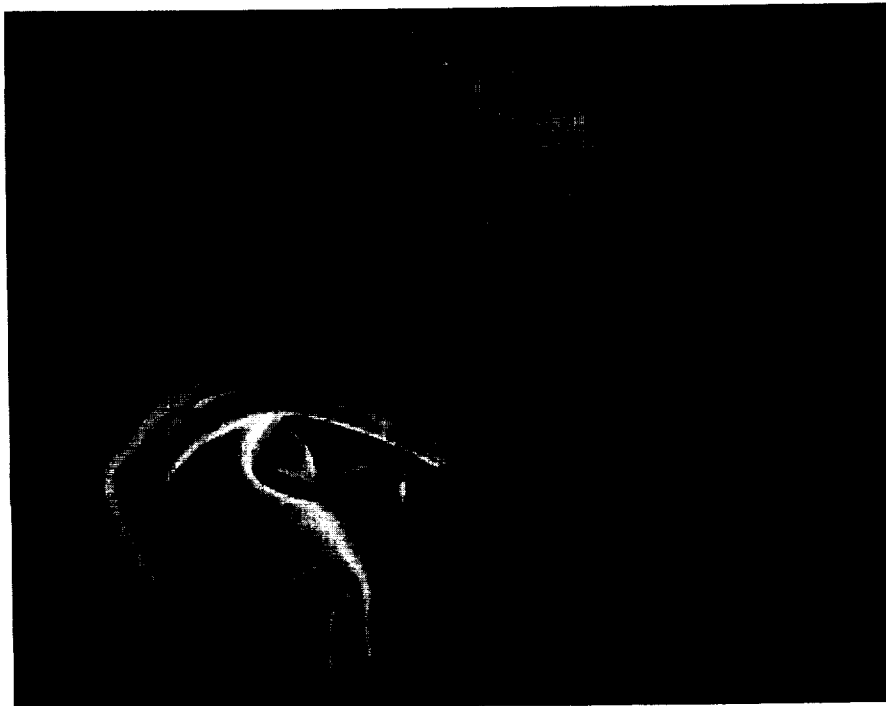
The metal to be sprayed was heated above its liquidus temperature and pressure-fed into a venturi-like nozzle transporting high velocity (mach number ~ 1.5) inert gas that also was heated to above the metal's liquidus temperature. Aerodynamic forces overcame the liquid metal's surface tension forces, resulting in a highly directed spray of finely atomized metal droplets. Outside the nozzle, the jet entrained relatively cold inert gas. This provided a heat sink for the spray, producing undercooled and semisolid droplets. The droplets were deposited onto a pattern that was manipulated in the jet to provide even coverage. The resultant metal shell was cooled to room temperature and separated from the pattern.

Results

Examples of spray-formed mold shells are given in Figure 6. Shells of tin (Figure 6a) and a zinc-base die-forming alloy (Kirksite, Figure 6b) were produced in about 5 min 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 shell at the deposit/pattern interface was measured to be as low as $2\ \mu\text{in}$ using a profilometer. As-deposited density, measured by water displacement using Archimedes' principle, has been close to 100% of theoretical for tin. The porosity



(a) Tin mold (right) and polyethylene pattern (left).



(b) Kirksite molds (left and above) and polyethylene pattern (right).

Fig. 6. Spray-formed metal mold shells.

distribution in a thin-sectioned mold shell is shown by the photomicrograph in Figure 7a. There is very little porosity through the thickness of the material. The grain structure of the same material is shown in Figure 7b. The equiaxed grain structure, with an average grain size of $9\ \mu\text{m}$ (ASTM grain size number 10 1/2), is much more refined than that of the cast starting material (Figure 7c) due to rapid solidification.

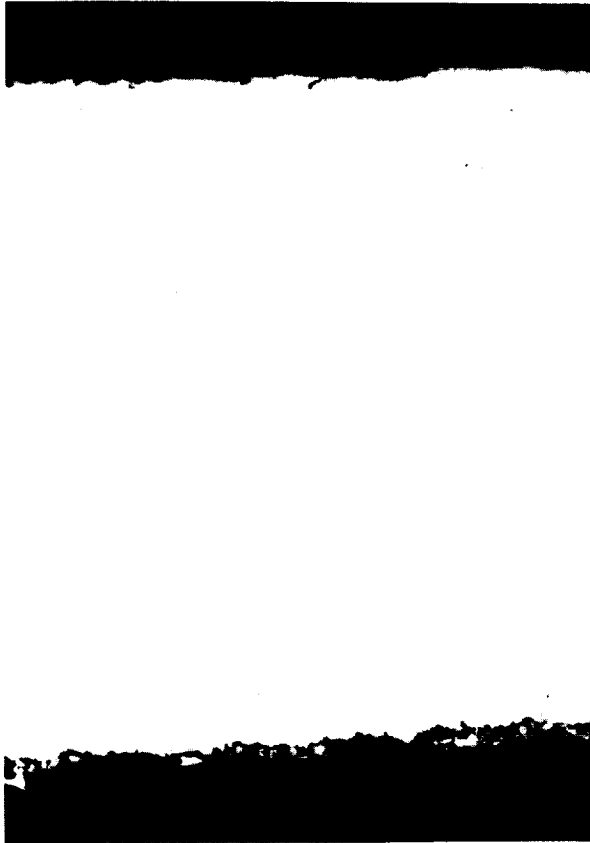
SEM analysis of overspray powder revealed that nearly all particles were spherical. Size analysis was performed using a laser aerosol spectrometer. Figure 8 gives the mass frequency of the tin and Kirksite alloy powders vs. size. The ordinate gives the mass frequency normalized for the channel size range, expressed as a percentage of the total mass. The mass median diameter was determined by interpolation of the cumulative weight vs. size data; it is the diameter corresponding to 50% cumulative weight (d_{50}). The Sauter (or area) mean diameter, d_{sm} , is sensitive to finer droplets, while the volume mean diameter, d_{vm} , is sensitive to coarser droplets. Together, they give a balanced view of the powder size. For tin, d_m , d_{sm} , d_{vm} , and the geometric standard deviation, $\sigma_v = (d_{84}/d_{16})^{1/2}$, were found to be $22\ \mu\text{m}$, $18\ \mu\text{m}$, $45\ \mu\text{m}$, and 2.4, respectively. For the Kirksite alloy these values were nearly identical: $22\ \mu\text{m}$, $18\ \mu\text{m}$, $44\ \mu\text{m}$ and 2.6, respectively. Increasing the mass loading by a factor of 5 to 100 lb/h while maintaining other spray parameters constant resulted in only a small increase in droplet size and size distribution. The type of atomizing gas (Ar, N_2 , and He) did not have a significant effect on atomization behavior at these mass loadings but may play a more important role in droplet quench rate and degree of undercooling.

ACKNOWLEDGMENTS

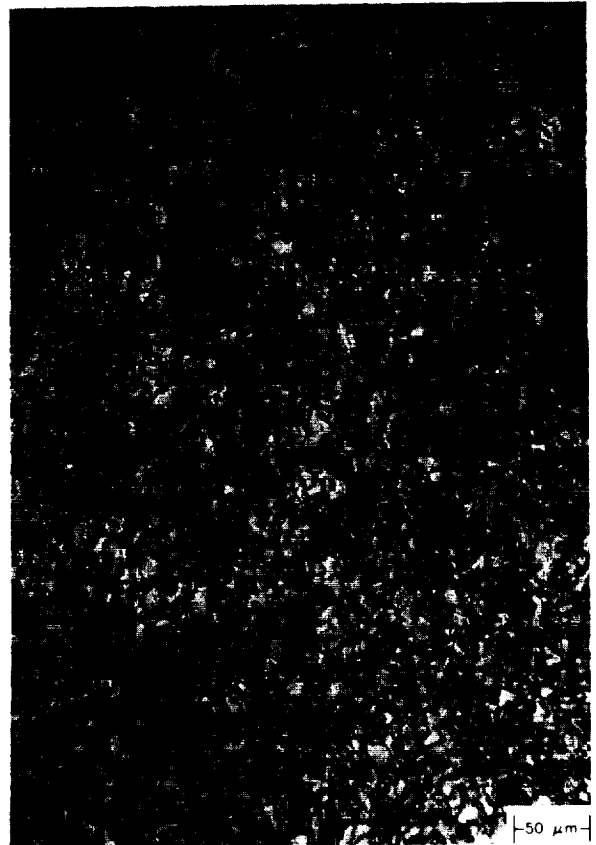
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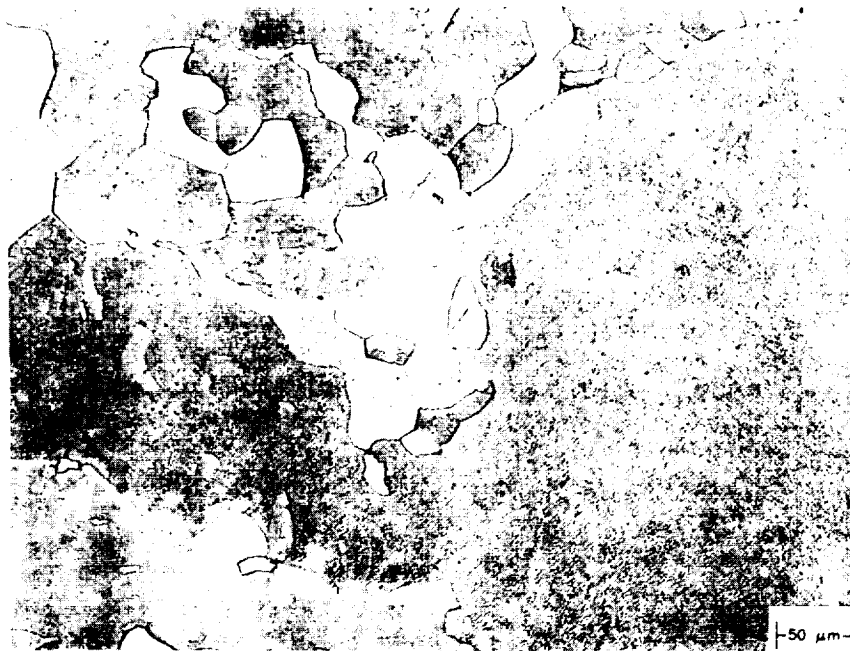
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(a) Spray-formed mold, polished.

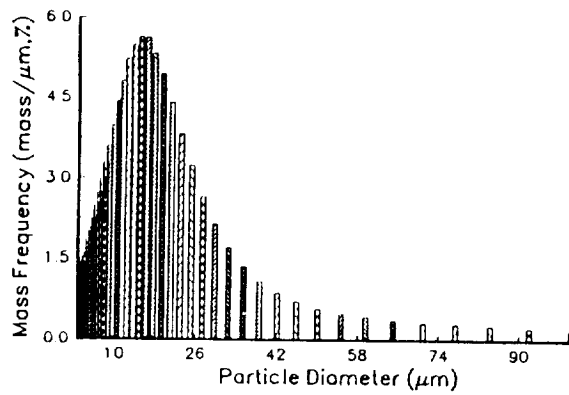


(b) Grain structure of spray-formed mold.

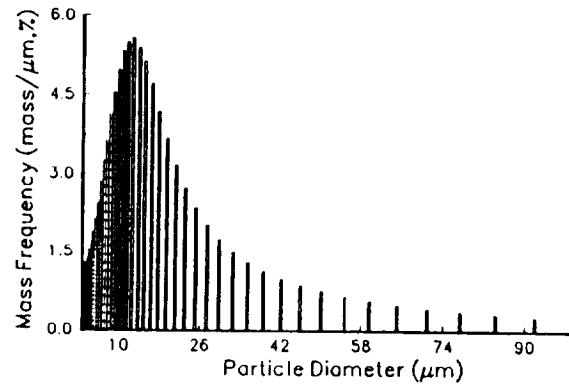


(c) Grain structure of cast metal.

Fig. 7. Photomicrographs of tin.



(a) Tin



(b) Kirksite alloy

Fig. 8. Mass frequency distribution of metal powders.

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