INL/CON-08-14352
PREPRINT

Density of Spray-Formed Materials

2008 World Congress on Powder Metallurgy & Particulate Materials

Kevin M. McHugh
Volker Uhlenwinkel
Nils Ellendt

June 2008

DENSITY OF SPRAY-FORMED MATERIALS

Kevin M. McHugh[1], Volker Uhlenwinkel[2] and Nils Ellendt[2]

[1]Energy Efficiency and Industrial Technology Department
Idaho National Laboratory
Idaho Falls, ID, USA 84415-2050

[2] Institute for Materials Science
University of Bremen
Bremen, Germany 28359

ABSTRACT

Spray Forming is an advanced materials processing technology that transforms molten metal into a near-net-shape solid by depositing atomized droplets onto a substrate. Depending on the application, the spray-formed material may be used in the as-deposited condition or it may undergo post-deposition processing. Regardless, the density of the as-deposited material is an important issue. Porosity is detrimental because it can significantly reduce strength, toughness, hardness and other properties. While it is not feasible to achieve fully-dense material in the as-deposited state, density greater than 99% of theoretical density is possible if the atomization and impact conditions are optimized. Thermal conditions at the deposit surface and droplet impact angle are key processing parameters that influence the density of the material. This paper examines the factors that contribute to porosity formation during spray forming and illustrates that very high as-deposited density is achieved by optimizing processing parameters.

INTRODUCTION

Spray Forming is an advanced materials processing technology that transforms molten metal into a near-net-shape solid. In spray forming, a stream of molten metal interacts with a high-velocity gas jet. Aerodynamic forces overcome the metal's surface tension forces producing an array of droplet sizes that are entrained by the gas jet and deposited onto a substrate. During their flight, the droplets cool at rates that depend on their size, thermodynamic properties, trajectory in the flow field, and other factors. Commercial applications include billets, rings, tubular products, and various flat products (sheet/plate) [1]. More recently, spray forming has been applied successfully to manufacture molds and dies [2-4], clad structures [5, 6] and tools to image micron-scale features into plastics and other materials[7].

All as-spray-formed materials contain some porosity. Values reported in the literature very early in the development of spray forming ranged from 15 vol. % to 20 vol. % and have steadily decreased over the years [8]. Hot deformation processing such as hot rolling, forging, extrusion and HIPping can eliminate porosity [8, 9]. However, these operations increase material cost and are not practical for some applications such as molds and dies. Porosity reduces mechanical properties such as strength [10, 11], ductility [12] elastic moduli [13-15] and toughness [16, 17] as well as electrical and thermal conductivity [18, 19]. While controlled levels of porosity may be desirable for some applications such as damping, insulation, energy absorption and weight reduction, a significant objective in spray forming is to minimize porosity [18].

Mechanisms of porosity formation in spray forming can parallel those in casting, i.e., gas entrapment and solidification shrinkage. Gas entrapment may result in randomly distributed, irregular pores or large, spherical pores if the liquid fraction at the deposition surface is too high [20]. Use of a gas that is soluble in the metal phase lessens the effect by reducing the partial pressure exerted by the gas or by forming secondary phase particles such as nitrides [8]. Solidification shrinkage is less commonly encountered in spray forming because a large amount of liquid is never present and the solidification front extends incrementally outward as the deposit builds up. It is sometimes found in the interior of large deposits such as billets.

In contrast to casting, interstitial porosity is rather common and results from incomplete filling of the interstices between droplet impacts as a deposit builds up [21]. Interstitial porosity typically forms during non-steady-state transients in processing conditions when the liquid fraction at the surface is too low. While it is most commonly found near the deposit/substrate interface and exposed surface of the deposit, random interstitial pores are found throughout the deposit.

While it is not feasible to achieve fully-dense as-deposited material, density > 99% of theoretical density is possible. This paper examines how substrate geometry, surface temperature, spray impact angle and metal composition contribute to porosity formation during spray forming and illustrates that as-deposited density > 99% of theoretical is achieved by minimizing processing transients and optimizing the spray and impact conditions during steady-state build-up. It also illustrates that 100% dense material is formed by integrating mechanical deformation into the spray forming process.

EXPERIMENTAL

A spray forming approach used at the University of Bremen is illustrated in Figure 1. A superheated molten metal stream issuing from a nozzle at the base of a preheated tundish is atomized using an annular array of gas jets. A constant metal level in the tundish and oscillation of the atomizer help maintain a uniform mass flux in the spray cone. An inert gas, typically nitrogen or argon, is used to atomize the metal and purge the inside of the closed vessel where deposition takes place to eliminate oxide inclusion defects in the deposited metal. The metal is collected onto a substrate that is manipulated in the spray to form flat products such as sheet and plate, tubular products and billets. This versatile approach can produce performs in most alloy systems including iron-based, aluminum-based and copper-based materials.

Another spray forming approach developed at the Idaho National Laboratory is illustrated in Figure 2. Molten metal is superheated about 100 K above the liquidus temperature and pressure-fed into the flow channel of a converging/diverging atomizer conducting a transonic to supersonic inert gas. The atomizing gas can be pre-heated to maintain the molten metal in a fluid state as it undergoes primary and secondary atomization inside the flow channel, and the multiphase flow is nearly fully developed prior to exiting the atomizer. Close-coupling of the metal and gas allows the atomizer to operate at a relatively low pressure (60 kPa above atmospheric pressure) and reduces the perturbing influence of the gas on the deposited metal. A conical spray (Fig. 2 b) is used to manufacture molds and dies by depositing the metal onto a tool pattern (substrate) (Fig. 2c). Figure 2d illustrates that this approach can image micron-scale features into the surface of metal. Flat products are manufactured by modifying the flow channel geometry to produce a fan spray (Fig. 16).

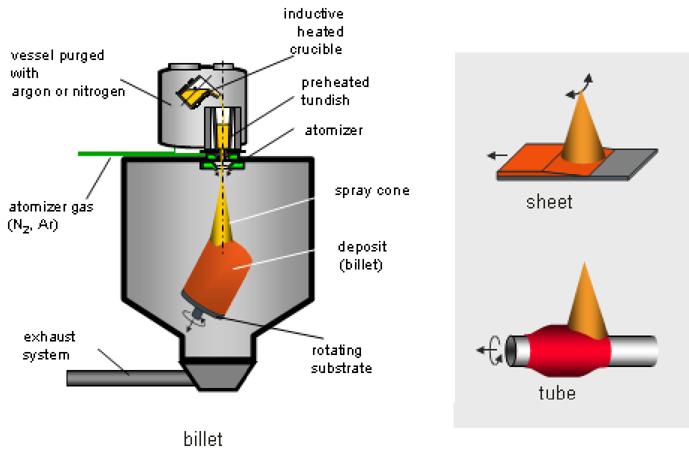

Figure 1. Principle of spray forming pre-forms: billet, tubes and sheet.

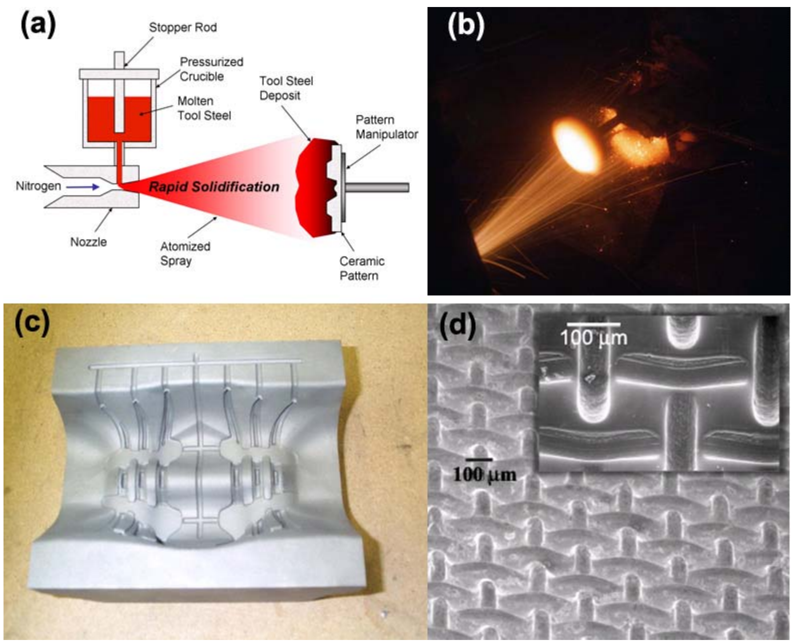

Figure 2. Spray forming molds and dies using a de Laval atomizer. (a) Schematic of approach. (b) Tool steel spray. (c) Spray formed P20 tool steel plastic injection mold insert for footwear. (d) Micron-scale features on a substrate (inset) were captured in the surface of spray-formed metal.

RESULTS and DISCUSSION

Substrate Geometry

A number of experimental investigations of porosity in as-sprayed material have been published in the past. In many studies, porosity was correlated with the liquid fraction of the droplets in the spray before they impact. In Figure 3, the average porosity of two different deposit shapes (billet and tube) and two different materials (IN 625 and Cu-6Ti) was correlated with the simulated average liquid fraction of the droplets. The average liquid fraction was calculated, and because this is based on a number of simplifications and assumptions, the absolute data cannot be compared with results from other models. Nevertheless, important conclusions can be drawn. For example, higher average liquid fraction of the droplets helps to reduce the porosity in both alloys. The porosity in the tube is much higher than in the billet for a given liquid fraction. This indicates that the liquid fraction in the spray is not the only parameter governing the porosity.

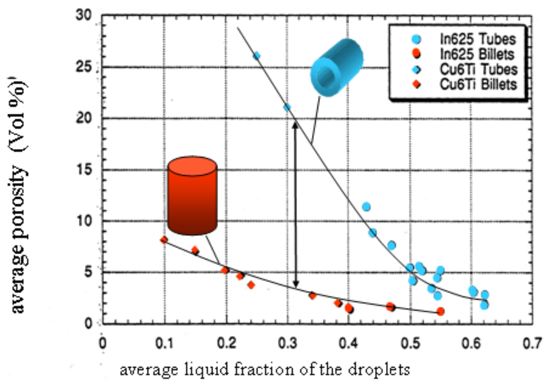

Figure 3. Average porosity in spray-formed billets and tubes versus average liquid fraction of the droplets, for two different alloys [22].

Experiments were conducted to quantify local porosity in spray-formed billets and tubes processed using similar spray conditions. In Figure 4, a bearing steel tube was spray-formed by sweeping a rotating tubular substrate through a stationary spray cone. The tube was sectioned and analyzed for porosity using image analysis at a resolution of 340 x 340 μm^2. Results are mapped in the color image of Figure 4 and indicate there is no appreciable gradient in the x-direction. Therefore, the values in x-direction were averaged and are plotted in the accompanying diagram. In contrast, a strong gradient was observed in the y-direction. The porosity level near the substrate is high (about 15%) but decreases to less than 1% in the interior of the deposit. Near the exposed surface, porosity again increases. The gradual decrease in porosity as the deposit thickness increases is attributed to a steadily increasing surface temperature. When a steady-state surface temperature is reached, the porosity remains relatively constant at <1%. This is followed by an increase in porosity near the exposed surface as the metal flux impacting the surface from the periphery of the spray cone, and spray liquid fraction, decrease resulting in a decrease in surface temperature.

The situation when spray forming a billet is quite different than spray forming a tube. After a relatively short spraying time the deposit's surface temperature reaches steady-state conditions. By scanning the spray cone over the surface of the billet, droplets from both the center and the periphery impact the same area of billet. This results in a more homogeneous mass and enthalpy flux at the surface. Figure 5 shows the relative density versus the radius of the billet for various gas-to-metal mass flow ratios (GMR). As was shown in Figure 3, a higher liquid fraction of the droplets (lower GMR) results in lower porosity. In the center region of the billet the porosity is low and almost constant (GMR = 1.2). However, near the edge of the billet, there is a sharp drop in density.

When spray forming a mold or die it is critical to minimize the duration of transients because it is the initial deposit that determines the quality of the mold's surface. Many molds have complex geometrical features which dictate the overall surface area on the tool pattern that must be covered. Due to rapid solidification, the pattern must be manipulated rapidly in the spray. For a single fixed spray cone, experience has shown that pattern manipulation using two independent rotational degrees of freedom and three coupled translational degrees of freedom is adequate to cover the surface. A relatively high liquid fraction in the spray is used initially to capture complex features on the tool pattern. The liquid fraction is then decreased during steady-state build-up.

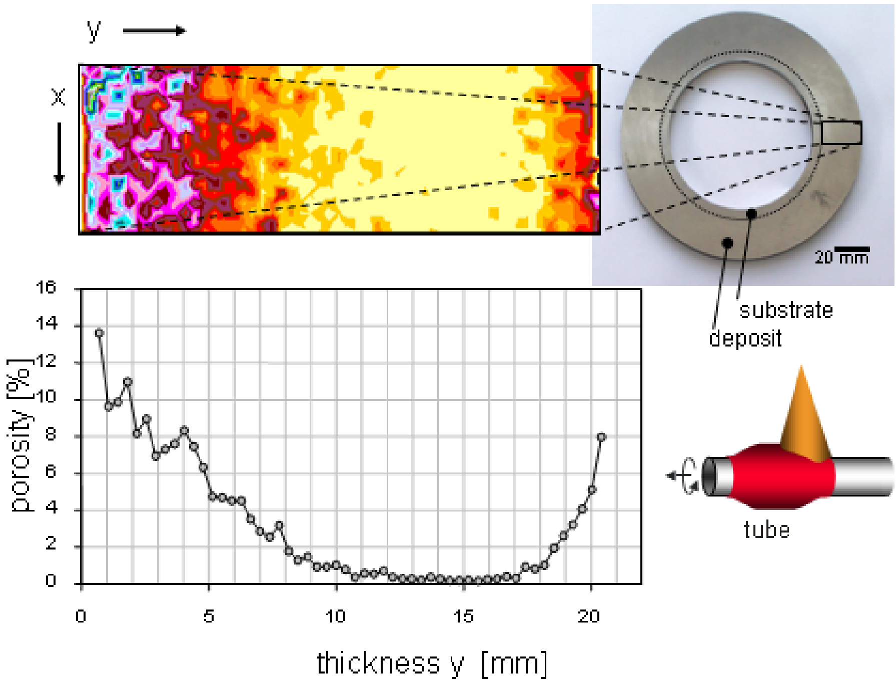

Figure 4. Local porosity in a spray-formed AISI 52100 bearing steel tube plotted against the thickness of the tube. Unheated, grit blasted substrate.

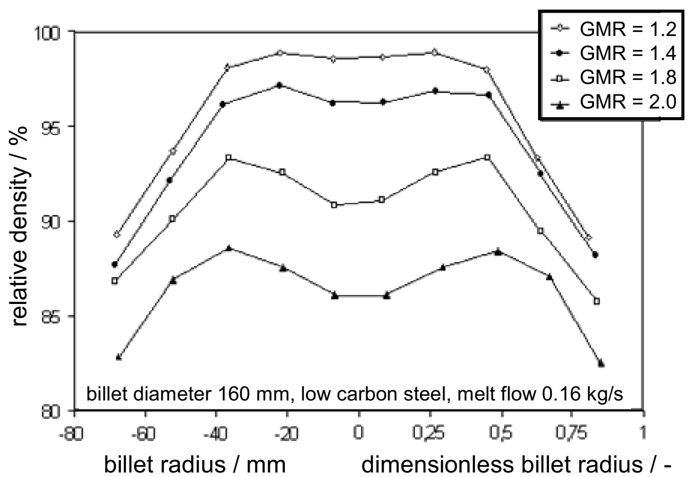

Figure 5. Relative local densities in a billet (low carbon steel, superheat = 160 K, gas flow 0.195, 0.224, 0.283, and 0.325 kg/s) [23].

Deposit Surface Temperature

When atomized droplets initially impinge upon a surface, momentum in the direction normal to the substrate is partially transferred to momentum in the radial direction. This transfer causes spreading and thinning of the droplet [24]. The dynamics of the spreading is very complex and depends on the size, liquid fraction, velocity, and impact angle of the particle as well as the roughness, temperature and reactivity of the surface. Figure 6 illustrates spreading behavior of atomized droplets of Zn-4Al-3Cu alloy (liquidus temperature 372 ^{O}C). The metal was heated to 500 ^{O}C and atomized with nitrogen heated to 500 ^{O}C. Droplets impacted a smooth glass substrate that was heated to temperatures ranging from 20 ^{O}C to 500 ^{O}C and rapidly swept through the spray zone to collect a small number of droplet impacts.

Preheating the substrate reduced the heat transfer rate. At low substrate temperatures (20 ^{O}C and 100 ^{O}C), droplet spreading was impeded due to viscous effects of the solidifying droplets. This resulted in an irregular edge, “orange-peel” surface and delamination. As the substrate temperature increased to ≥200 ^{O}C, interfacial tension was reduced and droplet spreading and adherence to the substrate improved. Note that small droplets co-deposited with the larger ones did not spread after impact indicating a low liquid fraction.

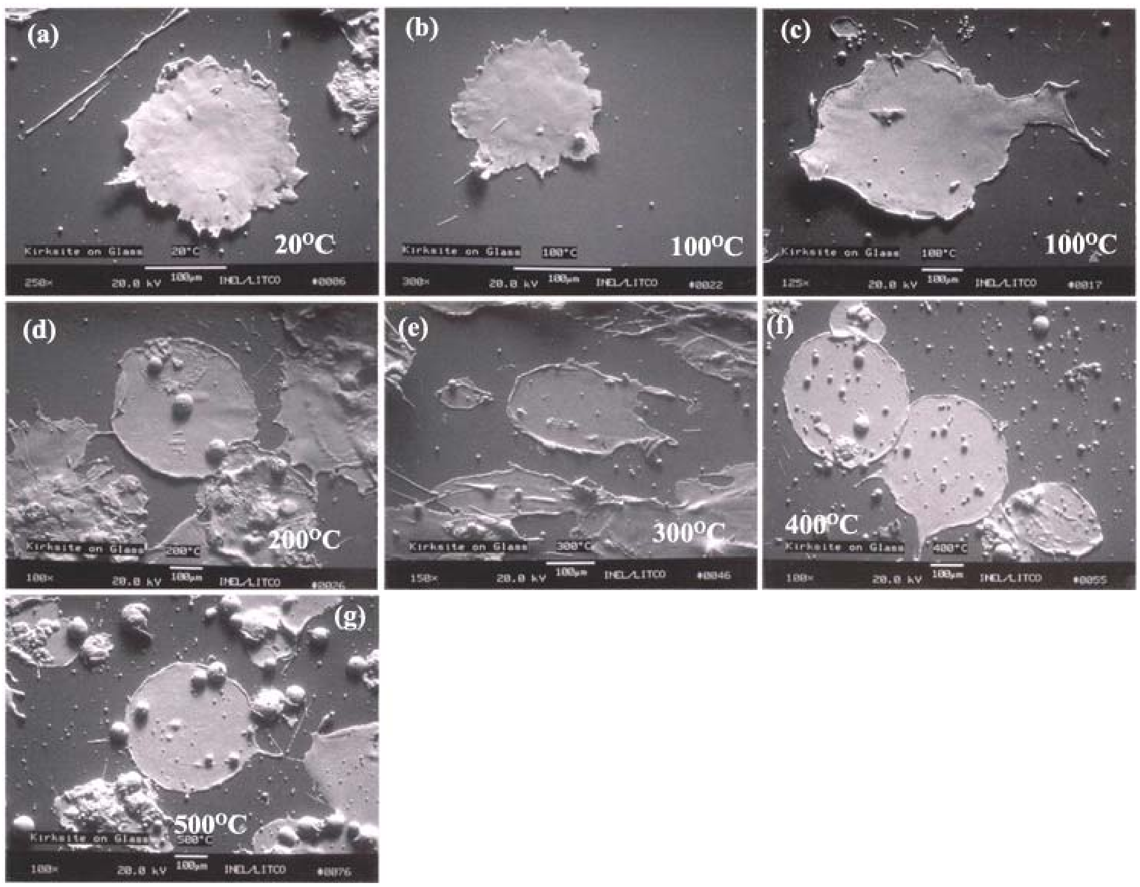

Figure 6. Zn-4Al-3Cu droplet impacts onto heated glass substrates. Substrate temperatures were (a) 20 ^{O}C, (b) 100 ^{O}C with “small” droplet impact, (c) 100 ^{O}C with “large” droplet impact, (d) 200 ^{O}C, (e) 300 ^{O}C, (f) 400 ^{O}C, and (g) 500 ^{O}C.

To investigate the influence of the deposit surface temperature on the local porosity in the spray formed material, a scanned spray of IN 718 was deposited onto a cylindrical steel substrate rotating at a frequency of 1.2 Hz. The temperature of the deposit surface was measured with a two-color pyrometer. The deposit was sectioned and polished. Porosity was evaluated by image analysis (each value based on an area of 0.1 mm^2) and correlated with surface temperature. Results are summarized in Figure 7. Porosity was minimized for deposit surface temperatures in the range of 1200 to 1250 °C.

The same experimental set-up was used to spray form Cu-15Sn alloy onto a steel substrate preheated to a temperature above the solidus temperature of the sprayed alloy. A photomicrograph of the polished deposit is shown in Figure 8. Porosity in the sprayed deposit was less than 1 vol.%, with a maximum pore diameter less than 20 µm. The sprayed alloy did not delaminate from the substrate following deposition and cold deformation.

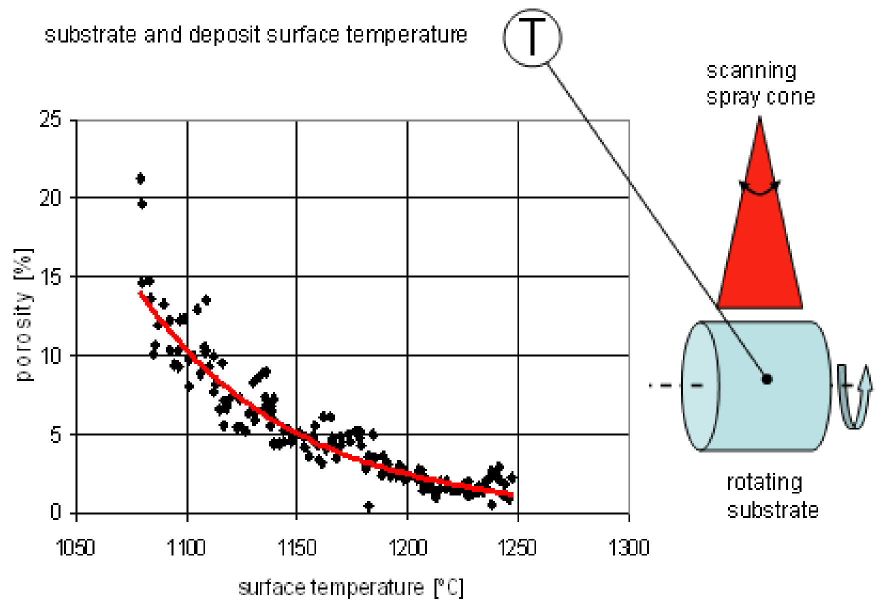

Figure 7. Relationship between porosity and deposit surface temperature of a spray formed superalloy (IN718).

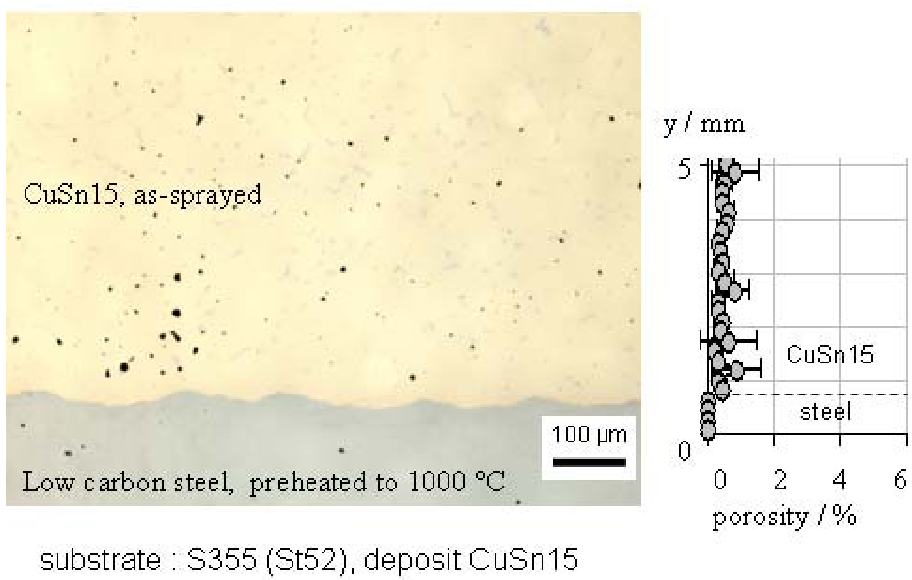

Figure 8. Photomicrograph at the interface of Cu-15Sn deposited onto a preheated steel substrate. The cross section of the layered material at the deposit/substrate interface is shown along with the measured porosity profile through the deposit.

Surface porosity in spray-formed molds and dies can't be tolerated because the mold is used with little if any surface preparation or benching. Porosity at the mold's surface could result in the transfer of flaws to the surface of molded components and interfere with their ejection from the mold. As described above, a high liquid fraction at the interface is beneficial for reducing porosity provided the spray does not erode the pattern material or degrade the metallurgical quality of the deposit. Figure 9a shows a sectioned AISI A2 tool steel (Fe-1.0C-0.85Mn-0.35Si-5.25Cr-1.1Mo-0.25V) deposit. The steel was induction melted under a nitrogen atmosphere, superheated about 100 K, and atomized with nitrogen using a bench-scale atomizer operating at a pressure of 60 kPa above atmospheric pressure and a metal discharge rate of 45.4 g/s. Density was evaluated by water displacement using Archimedes' principle and a Mettler balance (Model AE100). Density was also evaluated using optical microscopy in conjunction with Analysis™ software on polished and un-etched samples. Density of samples sectioned from near the deposit/substrate interface, center and near the exposed surfaces were similar with an average density of 99.7% of theoretical. Image analysis and water displacement measurements were similar. The accompanying photomicrographs at the deposit/pattern interface (Fig. 9b), exposed surface (Fig. 9c) and interior of the deposit (Fig. 9d) illustrate that low porosity through the deposit can be attained by preheating the pattern to lower the droplet/surface interfacial tension and promote wetting while maintaining a uniform surface temperature during build-up of the deposit.

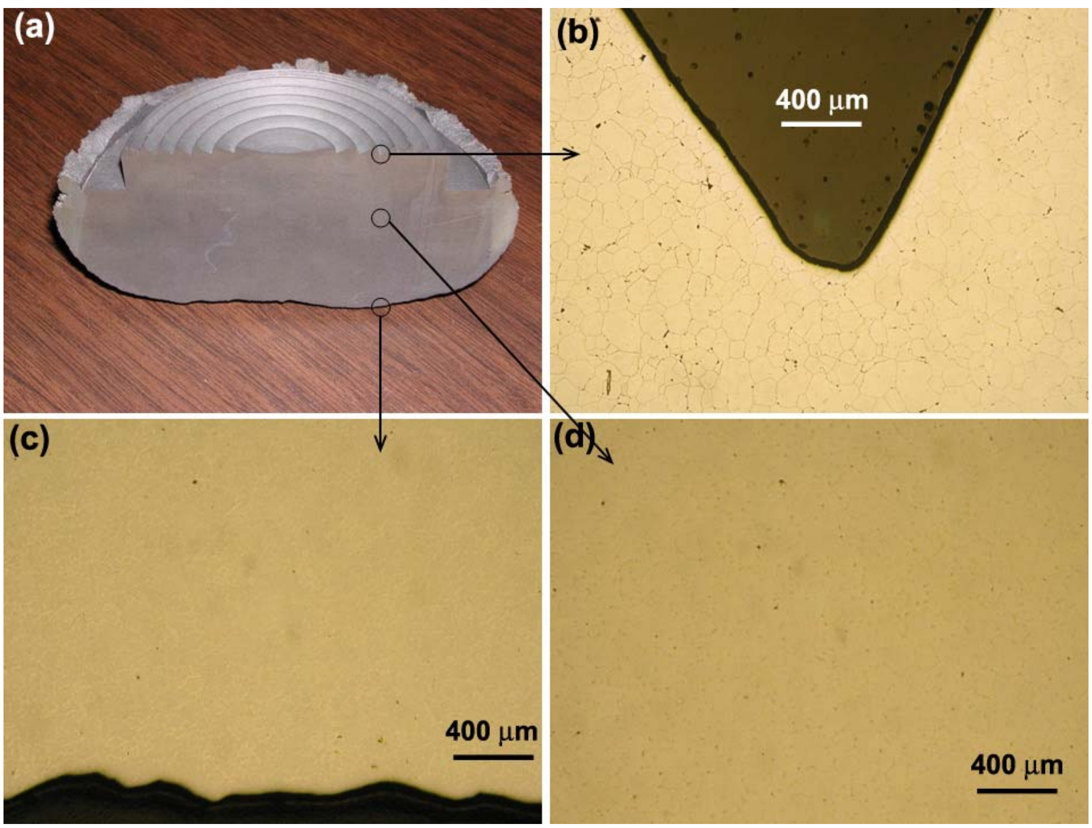

Figure 9. Microstructure of an A2 tool steel mold using a pre-heated substrate. (a) Sectioned mold. (b) Deposit/substrate interface, nital etch. (c) Exposed surface, polished. (d) Interior, polished.

When producing clad metal structures by spray forming, preheating the surface of the substrate (base metal) helps to promote metallurgical bonding by encouraging inter-diffusion as well as limit porosity at the interface which would weaken the bond strength. Energy dispersive spectroscopic analysis of the interface in AISI H13 tool steel, M2 tool steel, and A2 tool steel claddings with 4340 steel substrates indicate the bonds are metallurgical only if the base metal is pre-heated. A bulk deposit and photomicrographs at the interface are shown in Figure 10. Also shown (Fig. 10b) is the interface of a near-eutectic glass-forming steel (SHS727) spray clad to 1008 steel.

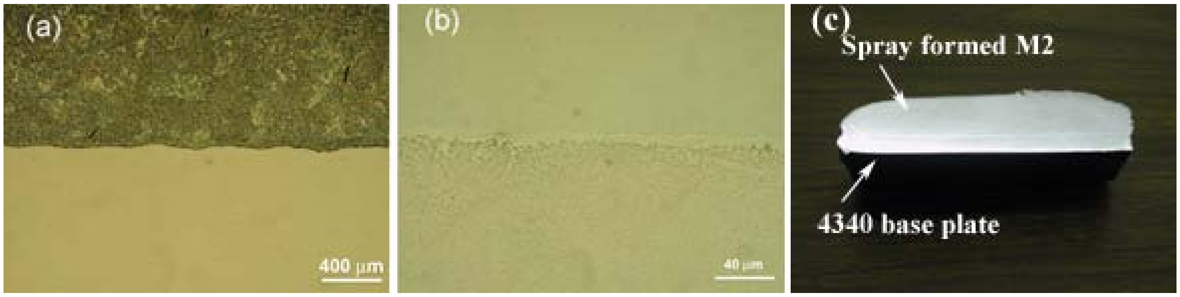

Figure 10. Photomicrographs of clad deposits. (a) spray formed A2 tool steel (lower deposit in figure)/4340 steel clad. 3% nital etch. (b) Spray-formed SHS 727 (a glass-forming steel)/1008 steel clad. As-polished. (c) As–deposited M2 tool steel/4340 steel clad.

Spray Impact Angle

To study the influence of the impact angle a ring was spray formed with the same experimental set-up depicted in Figure 7. Scanning the atomizer resulted in an "M" shaped deposit with maxima corresponding to the turn points of the spray cone. The white arrows in Figure 11 show the direction of the droplet velocity vector if we assume that all droplets start at the same point and follow a straight trajectory. The figure shows the cross-section of the ring (left) and weighted and average impact angle (right). The dark area to the left of the deposit marks a zone with high porosity. The impact angle is weighted by the local particle mass flux. Here, 0° impact angle is defined as a droplet trajectory perpendicular to the deposit surface. This comparison shows that there is a correlation between the high porosity zone and large impact angles.

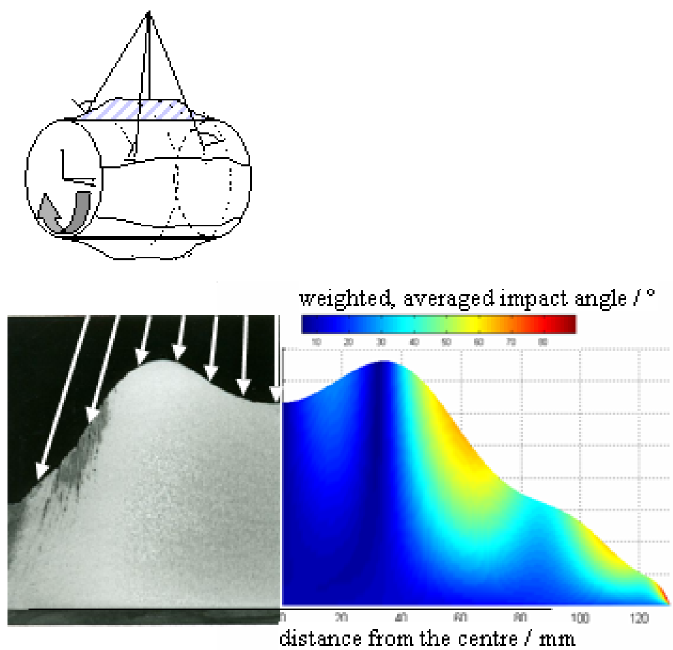

Figure 11. Effect of the average impact angle on the porosity of a spray-formed ring of IN718. Deposit cross section (left) and average impact angle (right).

Figure 12 illustrates the importance of spray impact angle when forming molds. AISI H13 tool steel (Fe-0.40C-5.00Cr-1.10V-1.30Mo) was deposited onto a preheated ceramic (alumina) tool pattern with the spray directed normal to the surface of the ceramic. The average density of the deposit was 99.5% of theoretical density. In contrast, material formed from droplets that impacted the edge of the ceramic at grazing angles was very porous. This is because initial metal build-up along the edge shrouded later droplet impacts resulting in a "feathering" effect.

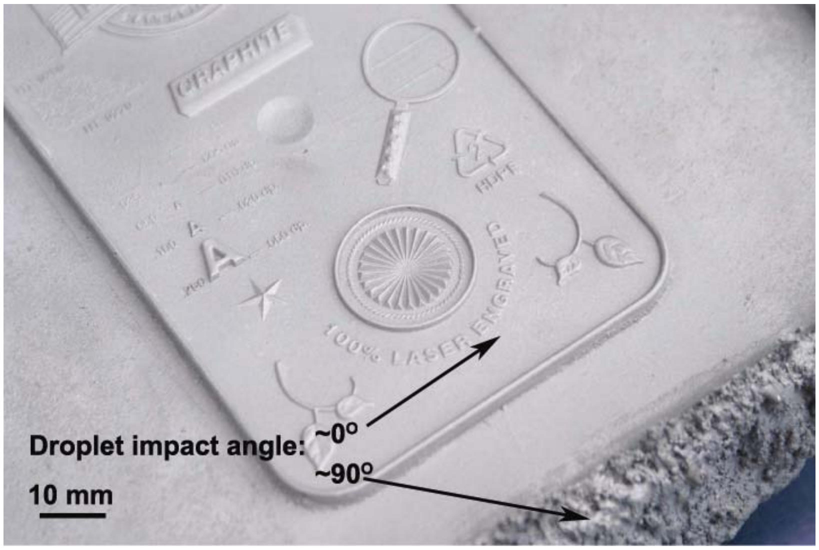

Figure 12. H13 tool steel deposit illustrating the influence of droplet impact angle on detail transfer from the substrate.

Six IN 718 rings (run numbers 338 – 343 in Fig. 13) were spray formed with an inner diameter of 340 mm. Porosity was measured by water displacement using Archimedes' Principle on cube-shaped samples (10 mm edge length) and correlated with the weighted, averaged impact angle. The porosity was low when the impact angle (measured relative to the normal to the surface) was less than about 20°.

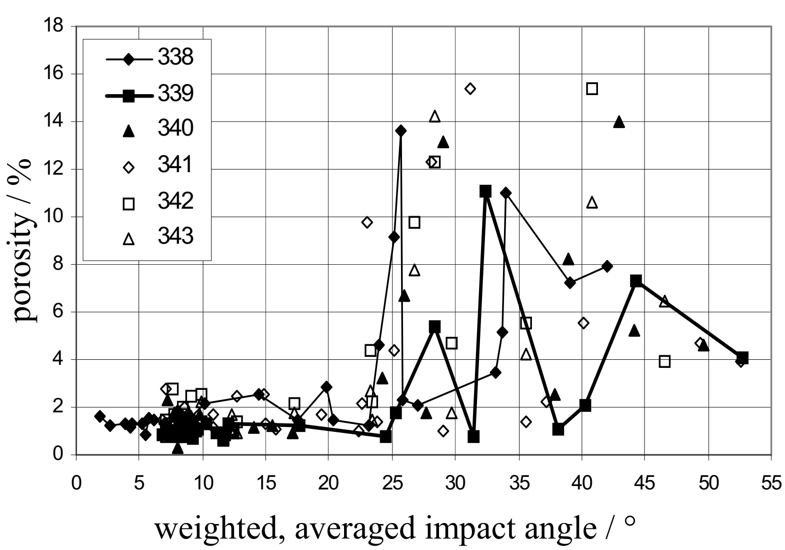

Figure 13. Porosity in spray-formed IN 718 rings as a function of average spray impact angle.

Sprayed Alloy Composition

The solubility and reactivity of the atomizing gas and molten alloy during deposition also influences porosity formation. Figure 14 summarizes the relative density of fourteen spray-formed alloys consisting of Al-Mg-Si-Cu alloys (black bars in Figure 14), Al-Si alloys (red bars), IN718 (blue bars), a bearing steel (gray bar) and Cu-based alloys (green bars). The highest density (greater than 99.5 %) was achieved for the bearing steel (Fe-1.5 Cr-1 C) [25].

IN718 was atomized with nitrogen and argon [26]. In both cases the density is >99% of theoretical. A higher density is achieved using nitrogen gas because the gas is somewhat soluble in the molten alloy. Nitrogen trapped in pores is absorbed during solidification which reduces the volume of the pores.

The as-deposited density of Al-Si alloys was >99 % for silicon additions of 18 wt. % and 25 wt.%. A 35 wt.% alloy, however, had a lower density (97% of theoretical). The low porosity of the alloys with 25 wt% or less Si leads to good formability during pressing, and it is also possible to draw wires with these alloys [27].

Al-Mg-Si-Cu alloys (with 15 to 20 wt.% Mg) can be spray formed with relative density of 98 and 97 %. An increase of the Mg and Si content leads to higher porosity.

Cu-based alloys (Cu-Al-X, Cu-Sn-X und Cu-Mn-Ni) without Ti additions are between 97 and 98% of theoretical density when atomized with nitrogen [28]. A small addition of Ti (0.25 wt %) increases the density substantially. As shown in Figure 14, this was true for three different Cu-based alloys. Other material properties are not affected. Ti reacts with nitrogen and forms TiN precipitates which reduces the overall nitrogen pore volume.

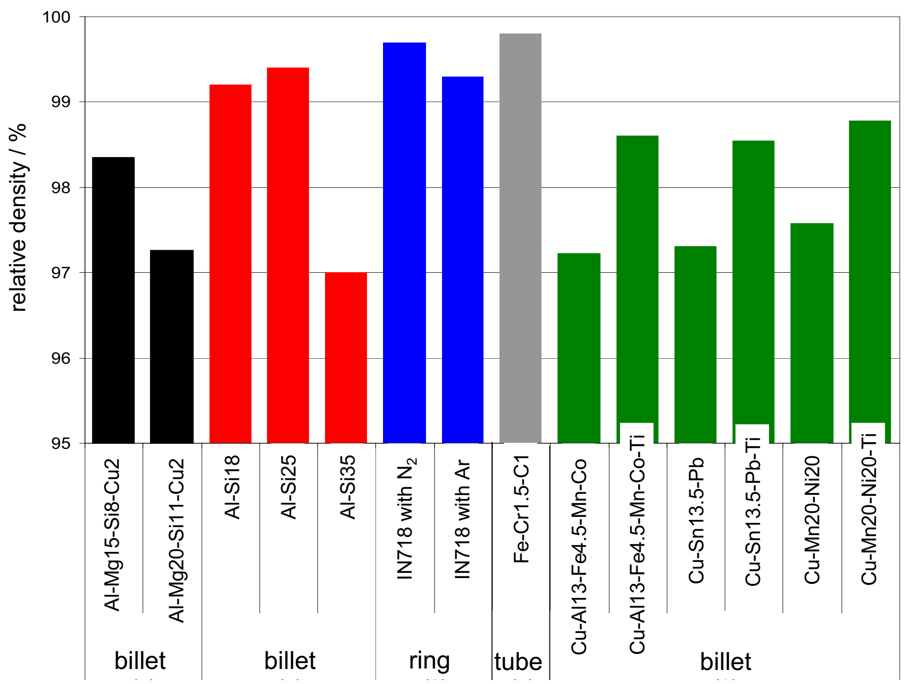

Figure 14. Relative densities of different alloys in the as-sprayed condition.

Integrative Processing

Spray forming processes that integrate hot deformation can be used to ensure full density. An example for manufacturing strip, *spray rolling,* is given in Figure 15. In this approach, the atomized spray is deposited into the nip of a pair of counter-rotating mill rolls. The contour of the rolls helps to collect the sprayed droplets, funnel them toward the roll nip and compress the semi-solid material. The general concept was pioneered by A. R. E. Singer in the 1970s [29] and recently developed for aluminum strip [30, 31]. To evaluate microstructure evolution during spray rolling, the rolls and spray were stopped simultaneously during steady-state processing of AA2124 strip. The resulting wedge was sectioned and viewed with an Olympus Model PME-3 metallograph and a Philips XL-30 ESEM scanning electron microscope. Four distinct regions were identified in Figure 16:

1. Impact region where the spray is collected by the rolls.
2. Consolidation region where the semi-solid material is funneled and is initially compacted.
3. Hot rolling region near the roll nip.
4. Product strip downstream of the roll nip.

The impact region (Fig. 16a) is characterized by an equiaxed grain structure and random, isolated pores. In the consolidation region (Fig. 16b), a decreasing number of pores were found as the semi-solid material advanced toward the roll nip and began to be compressed. Porosity and other flaws were eliminated in the hot rolling region (Fig. 16c) at a point where the cross-sectional thickness was about twice the roll gap.

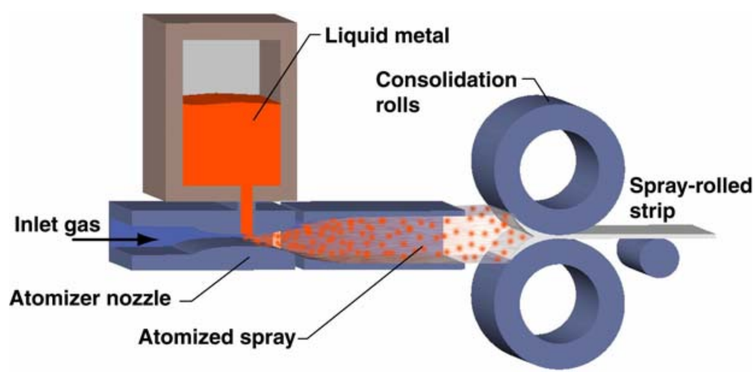

Figure 15. Schematic of spray rolling method to form metal flat products. Approach uses mill rolls to collect and consolidate atomized metal spray into fully-dense sheet metal.

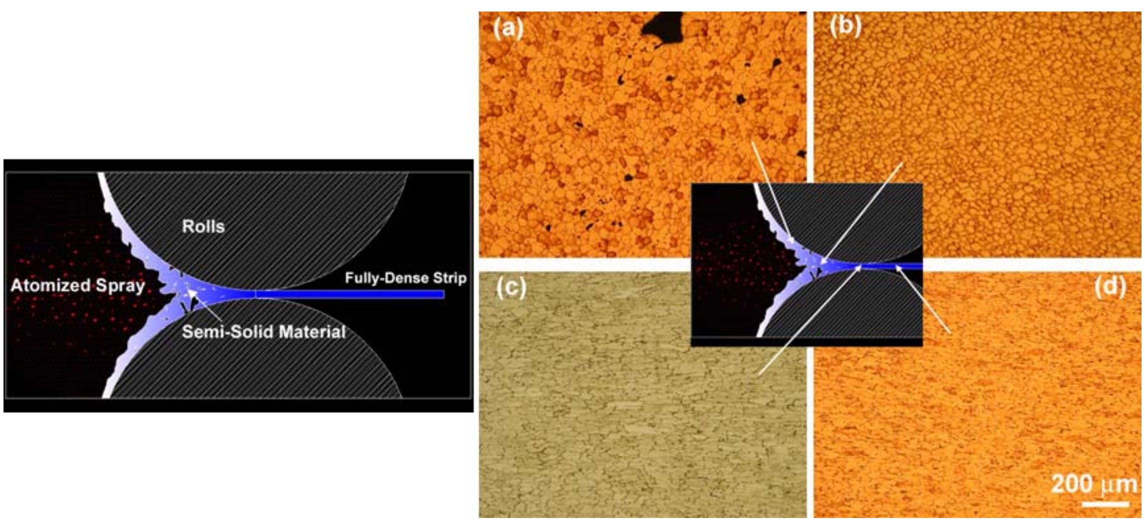

Figure 16. Microstructure evolution during spray rolling (a) Spray collection in the impact region. (b) Initial compaction of semi-solid material in the consolidation region. (c) Densification near roll nip. (d) Fully-dense strip exiting rolls.

It is important to control the liquid fraction of the deposited alloy at the impact region. Under optimized processing conditions, strips are free of porosity, segregation and other flaws as shown in

Figure 17 for AA2124 (Al-4.4Cu-1.5Mg-0.6Mn), AA7050 (Al-6.2Zn-2.3Mg-2.3Cu-0.12Zr) and AA5083 (Al-4.4Mg-0.7Mn-0.15Cr). However, if the fraction of liquid is too high, a solute-rich phase can be pushed to the surface of the strip forming a "surface bleed" as shown in Figure 18a for AA5083. Subsequent annealing resulted in vacancy porosity near the surface following diffusion of the solute-rich phase into the matrix (Fig. 18b).

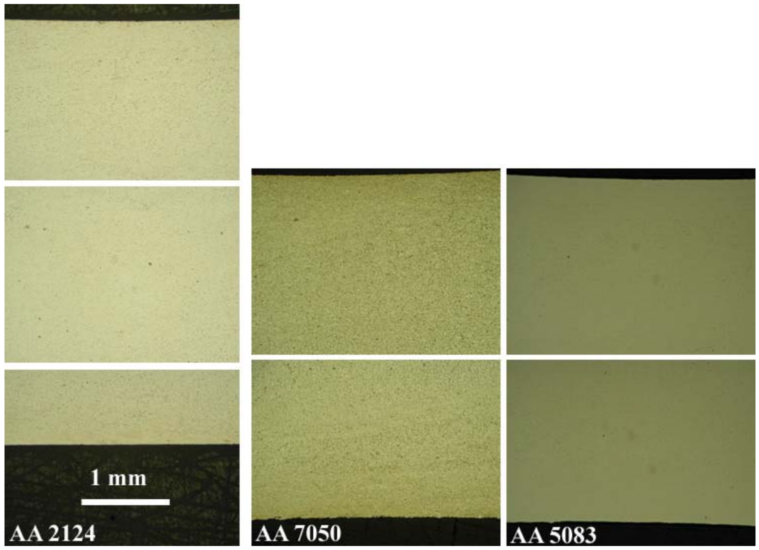

Figure 17. Spray-rolled strips of AA2124, AA7050 and AA5083.

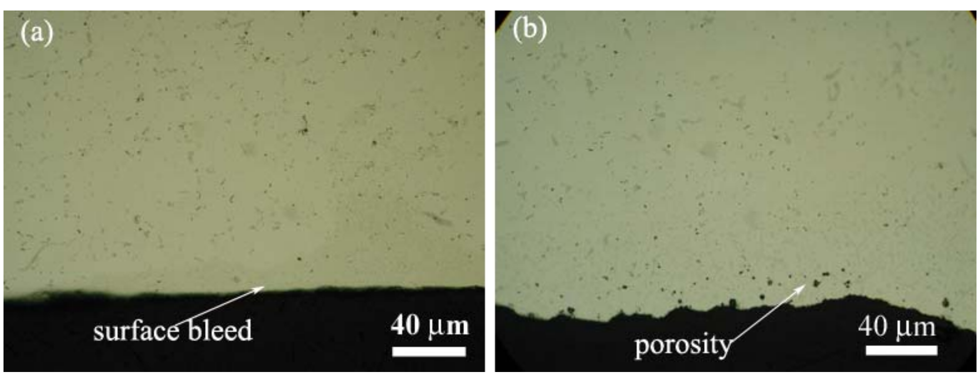

Figure 18. Spray-rolled AA 5083 processed with an unacceptably high liquid fraction during deposition. (a) High liquid fraction in deposit results in surface segregation of solute-rich phase during consolidation. (b) Kirkendall diffusion during annealing resulted in vacancy porosity [32].

CONCLUSIONS

- Spray forming can manufacture billets, tubular and flat products, molds & dies, and clad materials with as-deposited density >99% of theoretical density.
- The liquid fraction at the surface of the deposit plays a critical role in porosity formation. Optimal processing conditions take into account substrate geometry (surface area), deposit surface temperature, spray impact angle and other factors while minimizing transients.
- Integrative processes that incorporate in situ mechanical deformation with spray forming can generate fully dense material while retaining rapid solidification benefits.

REFERENCES

[1] A. Lawley, "Melt Atomization and Spray Deposition – Quo Vadis," *proceedings of SDMA 2000*, Bremen, Germany, June, (2000), 3-15.

[2] S. Hoile, T. Rayment, P. S. Grant, and A. D. Roche, "Oxide Formation in the Sprayform Tool Process," *Mater Sci. Eng. A* 383 (2004) 50-57.

[3] Y. Yang and H.-P. Hannula, "Development of Precision Spray Forming for Rapid Tooling," *Mater. Sci. Eng. A* 477 (2008) 63-68.

[4] K. M. McHugh, Y. Lin, Y. Zhou, and E. J. Lavernia, "Influence of Cooling Rate on Phase Formation in Spray-Formed H13 Tool Steel," *Mater. Sci. Eng. A* 477 (2008) 50-57.

[5] P. Chesney, "A New Spray Coating Process for Manufacture of Stainless Steel Clad Construction Steel with Resistance to Corrosion by De-Icing Salts & Seawater," *proceedings of SDMA 2003 and ICSF V*, Bremen, Germany, June, 2003, ch 5, pp. 3-9.

[6] K. M. McHugh and J. E. Folkestad, "Production of Molds and Dies Using the RSP Tooling Approach," *proceedings of SDMA 2003 and ICSF V*, Bremen, Germany, (2003) ch. 5, pp. 123-134.

[7] K. M. McHugh, "Advanced Manufacturing by Spray Forming: Aluminum Strip and Microelectromechanical Systems", *Proceedings of Technology 2004: The Fifth National Technology Transfer Conference*, Washington, DC, Nov., 1994.

[8] E. J. Lavernia and Y. Wu, *Spray Atomization and Deposition*, 1996, John Wiley & Sons, New York, NY.

[9] P. S. Grant, "Spray Forming," Prog. Mater. Sci. 39 (1995) 497-545.

[10] J. Kovacik, "The Tensile Behavior of Porous Metals Made by Gasar Process," *Acta. Mater.* 46 (15) (1998) 5413-5422.

[11] R. P. Baron, F. E. Wawner, and J. A. Wert, "Relationship Between Fractional Porosity and Tensile Strength for High-Porosity Sintered Ferrous Powder Compacts," *Scripta Mater.* 39 (3) (1998) 269-275.

[12] E. M. Dubensky and D. A. Koss, *Metall. Trans. A* 18 (1987) 1887-1895.

[13] M. Kupkova, "Porosity Dependence of Material Elastic Moduli," *J. Mater. Sci*. 28 (1993) 5265-5268.

[14] G. Straffelini, V. Fontanari, and A. Molinari, "True and Apparent Young's Modulus in Ferrous Porous Alloys," *Mater. Sci. Eng .A* 260 (1999) 197-202.

[15] J. Kovacik "Correlation Between Young's Modulus and Porosity in Porous Materials," *J. Mater. Sci. Lett.* 18 (1999) 1007-1010.

[16] G. Straffelini, V. Fontanari, and A. Molinari, "Impact Fracture Toughness of Porous Alloys Between Room Temperature and -60^{O}C," *Mater. Sci. Eng. A* 272 (1999) 389-397.

[17] G. Straffelini, A. Molinari, and H. Danninger, "Impact Notch Toughness of High-Strength Porous Steels," *Mater. Sci. Eng. A* 272 (1999) 300-309.

[18] P. S. Liu and K. M. Liang, "Functional Materials of Porous Metals Made by P/M, Electroplating and Some Other Techniques," *J. Mater. Sci.* 36 (2001) 5059-5072.

[19] P. S. Liu, T. F. Li, and C. Fu, "Relationship Between Electrical Resistivity and Porosity for Porous Metals," *Mater. Sci. Eng. A* 268 (1999) 208-215.

[20] M. G. Chu, "Microstructure of Aluminum Alloy Deposits Produced by Spray Forming Using a Linear Nozzle," *proceedings of the Third International Conference on Spray Forming,* Cardiff, UK, (1996) 27-35.

[21] S. Annavarapu and R. Doherty, *Int. J. Powder Metall.*, 29 (1993) 331.

[22] L. Warner, C. Cai, S. Annavarapu, R. Doherty: Modelling Microstructural Development in Spray Forming: Experimental Verification. *Proc. ICSF III*, Cardiff, UK (1996) pp 265-272.

[23] Buchholz M: Untersuchung des Kompakierverhaltens an sprühkompaktierten Bolzen, Dissertation, Universität Bremen 2002.

[24] J. -P. Delplanque, E. J. Lavernia, and R. H. Rangel, "Multi-Directional Solidification Model for the Description of Micro-Pore Formation in Spray Deposition Processes," *Numerical Heat Transfer, Part A: Applications*, 30 (1996) 1.

[25] Schulz A., V. Uhlenwinkel, M. Buchholz: Kontrollierte Wärmezufuhr zur Beeinflussung von Homogenität und Haftung sprühkompaktierter Rohre aus Stahl. Abschlussbericht, AiF-Projekt 12727N, 2003.

[26] Uhlenwinkel, V.; R. Attwater, L. Achelis, M. Walter: Spray Forming of Superalloy Rings. Proc. PM 2004, Wien, Austria, Vol.5, S. 33-38.

[27] Cui C., A. Schulz, K. Schimanski, H.-W. Zoch, P. Baumgart, F. Syassen, R. Kocik: Development of New Filler Materials for Welding of Aluminium Structures by Spray Forming. In: The Bremen Production Days", *proc. International Conference on Applied Production Technology 2007* (APT´07), Bremen 17-19 Sept. 2007, Ed. F. Vollertsen u.a.

[28] Müller H.R., K. Ohla, R. Zauter, M. Ebner: Effect of Reactive Elements on Porosity in Spray-Formed Copper-Alloy Billets. *Mater. Sci. Eng. A* 383 (2004) 78-86.

[29] A. R. E. Singer, *Met. Mater.* 4 (1970) 246.

[30] K. M. McHugh, J.-P. Delplanque, E. J. Lavernia, Y. Zhou and Y. Lin, " Spray Rolling Aluminum Strip," *Mater. Sci. Eng. A* 383 (2004) 96-106.

[31] K. M. McHugh, Y. Lin, Y. Zhou, S. B. Johnson, J.-P. Delplanque and E. J. Lavernia, "Microstructure Evolution During Spray Rolling and Heat Treatment of 2124 Al," *Mater. Sci. Eng. A* 477 (2008) 26-34.

[32] K. M. McHugh, E. J. Lavernia, Y. Zhou, Y. Lin, J.-P. Delplanque and S. B. Johnson, "Spray Rolling Aluminum Strip—Process Development and Strip Properties," proceedings of the *Symposium on Hot Deformation of Aluminum Alloys III,* 2003 TMS Annual Meeting, San Diego, CA March, 2003, ed. Z. Jin, A. Beaudoin, T. A. Bieler, and B. Rhadhakrishnan,(2003) pp 443-452.