1999 June
Report No. C97-3411-FINAL

ALCOA TECHNICAL CENTER
100 TECHNICAL DRIVE • ALCOA CENTER, PA 15069-0001

Spray Forming - Aluminum

Final Report (Phase II)

Submitted to:
U. S. Department of Energy

Submitted by:
Alcoa Inc.
Alcoa Technical Center
100 Technical Drive
Alcoa Center, PA 15069-0001

ALCOA

Creating Value through Technology

DISCLAIMER

Spray Forming - Aluminum

Final Report
(Phase II)

1999 June

Work Performed Under Contract:
DE-FC07-94ID13238

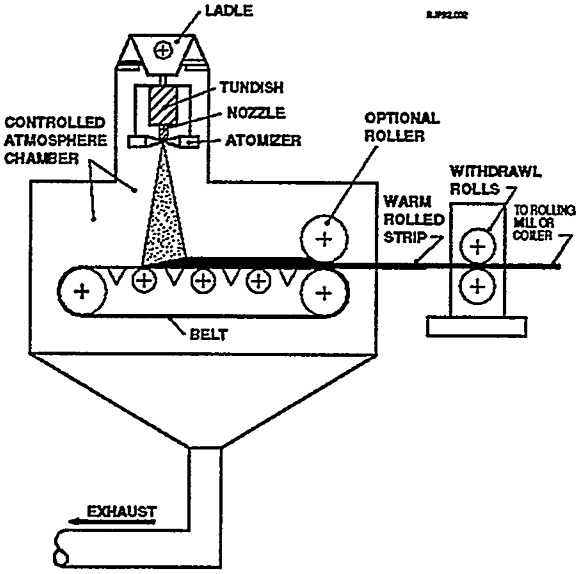
Reported by:
David D. León
Program Manager

Prepared for
U.S. Department of Energy
Field Office, Idaho Falls, ID
Sponsored by the Office of the Assistant Secretary for
Energy Efficiency and Renewable Energy
Office of Industrial Technologies
Washington, D.C.

Prepared by
Alcoa Inc.
Alcoa Technical Center
100 Technical Drive
Alcoa Center, PA 15069-0001

ABSTRACT

The U.S. Department of Energy - Office of Industrial Technology (DoE-OIT) has an objective to increase energy efficiency and enhance competitiveness of American metals industries. To support this objective, Alcoa Inc. entered into a cooperative program to develop spray forming technology for aluminum. This Phase II of the DoE Spray Forming Program would translate bench scale spray forming technologies into a cost-effective, world class process for commercialization.



Developments under DoE Cooperative Agreement No. DE-FC07-94ID13238 occurred during two time periods due to budgetary constraints: 1994 April through 1996 September and 1997 October through 1998 December. During this period, Alcoa Inc. developed a linear spray forming nozzle and specific support processes capable of scale-up for commercial production of aluminum alloy sheet products. Emphasis was given to 3003 and 6111, commercially significant alloys in the automotive industry.

The enclosed report reviews research performed in these areas:

- Nozzle development
- Deposition
- Computer simulation
- Fabrication
- Material characterization
- Economics

With the formation of a Holding Company, all intellectual property developed in Phases I and II of the Project have been documented under separate cover for licensing to domestic producers.

TABLE OF CONTENTS

Page No.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

0.0 BACKGROUND / INTRODUCTION

0.1 Metals Initiative Act and Phase I Results

There is a critical need for efficient, inexpensive, reproducible metal production processes that use less energy and generate less environmental contamination. Currently, to obtain higher added value and less cost, the metals industry is moving away from capital-intensive processing towards flexible manufacturing processes.

The Department of Energy (DoE) is managing the Steel and Aluminum Energy Conservation and Technology Competitiveness Act of 1988 to "reestablish an industrial energy conservation and competitive technology program to conduct scientific research and development of steel and aluminum technologies." Research and development projects were funded to increase the energy efficiency and enhance the competitiveness of American steel, aluminum, and copper industries.

Near-net-shape casting of plate/sheet preforms holds potential cost reduction benefits. As with other metals, continuous casting of aluminum is gaining acceptance for the production of low-alloy sheet products replacing the more conventional processes.

Spray forming is a near-net-shape casting technology based on atomization of liquid melts and subsequent deposition on a substrate. Rapid solidification occurs resulting in beneficial effects of a refined microstructure and compositional homogeneity. Spray forming, as a means to manufacture aluminum sheet products was originally described by Singer [1]. Commercial production of sheet and plate by spray forming is a potentially attractive manufacturing alternative to conventional ingot metallurgy/hot-milling and to continuous casting processes because of reduced energy requirements and reduced cost. These significant advantages are achieved through the elimination of several process steps and lower capital costs. Further, the spray formed material is metallurgically superior to continuous cast materials because of the following characteristics:

- Uniform distribution of equiaxed grains (2-200 microns)
- No macroscopic segregation of alloying elements
- Uniform distribution of second phases
- Low oxide content
- Absence of powder particle boundaries

Figure 1 compares the three most common methods for manufacturing aluminum reroll stock.

During Phase I of the Program, projects for the development of a spray forming process for steel were conducted by the Department of Energy and a consortium of cost-sharing industrial participants. Three concurrent projects began in 1989 March at the Idaho National Engineering & Environmental Laboratory (INEEL), Massachusetts Institute of Technology (MIT), and Oak Ridge National Laboratory (ORNL). The three projects were primarily directed toward developing and evaluating different spray forming nozzle/atomizing technologies to produce low-carbon steel strip. Most spray-forming efforts before this program used round nozzles that resulted in low production rates, high losses caused by overspray and poor surface microstructure. Linear nozzle designs overcome these problems and were considered the design of choice. Results indicated that the USGA (Ultrasonic Gas Atomization) nozzle system from MIT and the deLaval type nozzle developed at Idaho National Engineering and Environmental Lab (INEEL) were ready for pilot plant evaluation with good potential for cost and energy savings over conventional processes. Phase I results demonstrated that spray forming should be investigated at the pilot plant scale to convert current technology into a viable commercial process. Although this program was directed towards steel, most of the information developed was applied to aluminum and served as a basis for the Alcoa work.

0.2 Alcoa Proposal & Program

To support DoE's objective to increase energy efficiency and enhance competitiveness of American metals industries, Alcoa entered into a cooperative program to develop spray forming technology for aluminum. This Phase II of the DoE spray forming program would translate bench scale spray forming technologies into a cost-effective, world class process for commercialization.

Developments under DoE Cooperative Agreement No. DE-FC07-94ID13238 occurred during two time periods due to budgetary constraints: 1994 April through 1996 September and 1997 October through 1998 December. Two Statements of Work (SOW) were developed for the Spray Forming of Aluminum Program corresponding to the two time periods. In addition two Work Breakdown Structures (WBS) were developed corresponding to these. Both have been included as Attachment I.

0.3 The Alcoa Spray Forming Team

The Alcoa Spray Forming Team was comprised of skilled scientists, technicians, and program managers who brought an excellent combination of experience, technical capability, and knowledge to support the program. These individuals were selected based on their thorough understanding of process development and fabrication of aluminum products; design and development of constitutive models; material science metallurgy; equipment design and operation; and program management. Their experience is broad-based having a proven capability for developing approaches and blending various disciplines to meet demanding technical requirements. Members of the Team included:

Program Manager	-	Frank W. Baker ('93-'96), David D. León ('96-present)
Principal Investigator	-	Robert L. Kozarek
Lead Operators	-	William D. Straub & Donald J. Stanko
Engineering/Design	-	Richard Slaugenhaupt / Thomas A. Egeland / Thomas R. Hornack
Nozzle Consultants	-	Ali Ünal, Jamal Righi
Solidification/Metallurgy	-	Men Glenn Chu
Modeling	-	S. John Pien

Thermo-Mechanical Processing - Ali I. Kahveci, Diana K. Denzer
Contract Administrator - Michael G. Plonsky / Sheree L. Haus / David R. Williams / Henry H. Guerke
Legal Counsel - Gary P. Topolosky

0.4 Subcontracts

Alcoa complemented its in-house expertise with outside consultants and subcontractors. Considerable work on spray forming equipment, spray nozzles, process control and modeling has been conducted by various companies, government laboratories and universities. Over the length of the project various sub-contractors and consultants contributed to the Alcoa Team as noted in Table 1.

Table 1-- Subcontractors and Consultants

Location	Principal Contacts	Major Activities
Air Products and Chemicals, Inc.	Mr. Mike Lanyi	Gas distribution system and analysis, controls, gas supplies
Carnegie Mellon University Department of Mechanical Engineering	Prof. Tom Shih	Modeling high speed gas dynamics
Carnegie Mellon University	Prof. Minking Chyu	Modeling gas / droplet interactions and shape
Carnegie Mellon University Combustion and Sprays Laboratories	Prof. Norman Chigier	Nozzle testing and spray diagnostics, design
Drexel University	Dr. Roger Doherty	Consultant - TMP development for 6111 sheet alloy, and analysis of final structure and mechanical properties
Idaho National Engineering and Environmental Laboratory (INEEL)	Dr. Kevin McHugh	Nozzle characterization of INEEL nozzle spray tests and deposit characterization
Massachusetts Institute of Technology	Prof. Merton Flemmings	Binary alloys studies, droplet undercooling, droplet impingement
Massachusetts Institute of Technology - Rapid Solidification Laboratory	Prof. Nicholas Grant	USGA nozzle design, metal spray test, speed photography
Massachusetts Institute of Technology - Edgerton Laboratory	Prof. Charlie Miller	High speed photography
Massachusetts Institute of Technology - Mechanical Engineering Dept.	Prof. J-H Chun	Characterization of droplet impact behavior under various droplet and deposit conditions

Table 1 -- Subcontractors and Consultants (cont'd)

Location	Principal Contacts	Major Activities
University of California - Irvine Department of Chemical Engineering and Material Science	Dr. Enrique Lavernia	Nozzle testing and metal spray diagnostic testing
Olin Corporation - Metals Research Laboratories	Dr. Derek E. Tyler	Expertise in process control, equipment design and process modeling with Osprey copper spray atomization system
University of Bremen (Germany)	Joern Fischer*	Spray plume characterization, in-line sensors

* Mr. Fischer performed his research at ATC as a student intern.

0.5 Program Milestones

Table 2 contains the Milestone Log for Phase II of the Spray Forming of Aluminum Program.

Table 2-- Milestone Log

Identification Number	Description	Planned Completion Date	Actual Completion Date	Comments
A1.1.1	Equipment modifications	6-30-94	12-31-93	Bench-scale spray forming equipment commissioned.
B.1.1.3	Numerical model assessment	9-30-94	9-30-94	Models now in place for use.
C1.1.3	Initial nozzle characterizations	12-31-94	12-31-94	Initial characterization on USGA and ALCOA nozzles complete. To continue in 1995.
D.1.3.1	Nozzle parametric study	6-30-95	6-30-95	Initial study on USGA, INEEL and ALCOA systems completed.
E.1.1.5	Feasibility of linear concept	4-18-96	12-31-96	NEW MILESTONE, based on revised SOW (8/95). Completed.
F.2.1	Complete Advanced Development Unit (ADU) design	12-07-98	N/A	Project terminated in 1998.
G.3.1.1	ADU operating parameters	5-14-99	N/A	Project terminated in 1998.
H.2.5.3	ADU commissioned	7-16-99	N/A	Project terminated in 1998.
I.3.3.2	Sheet produced for market evaluation	1-31-00	N/A	Project terminated in 1998.

1.0 IMPROVE PROCESS UNDERSTANDING AND CAPABILITY

To meet the program's commercialization objectives, a set of critical technical goals were established, as follows:

- Obtain ± 2% thickness variation across the as-deposited layer (exclusive of edge effects).
- Eliminate interconnected porosity in surface layers next to the substrate or top surface. No scalping or other mechanical processing should be required to the deposit top or bottom surfaces prior to subsequent rolling operations.
- Reduce overspray losses to less than 5%.
- Confine edge effect to less than 25 mm (1 in.) on each edge of the as-deposited layer.
- Demonstrate interruption and restart capability of the spray forming process. A five minute delay should have no discernible effect on finished product properties across the interface.
- Demonstrate that the spray forming process is in control by achieving a C_{pk} of 1.0 or more for critical parameters including: metal pouring rate, gas/mass flow rate, metal temperature, average droplet size, substrate motion and temperature, etc. This shows the process to be in control and capable of meeting stated requirements. The critical parameters will not deviate by more than ± 5% from nominal.

1.1 Equipment Development / Modifications

1.1.1 Conversion of the TAFA Thermal Spray Unit into a Spray Forming Unit.

The spray forming equipment at ATC was based on a converted TAFA plasma spray facility. A schematic is shown in Figure 2. The Unit consisted of a horizontal pressure/vacuum vessel 50 in. diameter x 100 in. long. Spray deposition occurred on a horizontal translating table capable of 190 in./min travel speed. Up to 50 lb aluminum melts were possible. The melt size allows spraying of deposits of up to 8 in. wide x 1 in. thick by 40 in. long. Spray times ranged from 30 seconds to nearly a minute. Dust control was via a Rotoclone type N, 8000 CFM max. wet scrubber.

Typically two video cameras are used to record spray runs. External lighting was provided through a port and a fiber optic system was installed to provide additional focused lighting inside the chamber.

1.1.2 Construction of the Mini-Spray Chamber

Alcoa developed a small scale spray chamber to facilitate studies with different alloys and to quickly perform screening tests. A mini-spray chamber was constructed by converting a Marko Spin Caster (See Figure 3) since the unit already shared many of the functions needed for a spray forming unit.

The basic Marko chamber is a stainless steel cylinder 20 in. in diameter by 20 in. long mounted horizontally with a large 20 in. door at one end. It has a small 2 lb capacity bottom pour induction heated crucible located in the top arm of the chamber. The unit has a full vacuum system. The substrate is stationary so the resulting deposit is typically Gaussian shaped. The nozzle is an axisymmetric version of the Alcoa III system so that nozzle parameters from the Marko unit can be directly related to the TAFA unit linear nozzle operation.

1.1.3 Furnace Redesigns

The original TAFA melting furnace used a graphite crucible with an induction coil. This later was replaced with radiant ceramic heaters mounted inside the top section of the spray forming vessel. The nozzle assembly bolts up to the furnace from below with the connecting drop tube providing the path for metal supply. Turnaround requires the disassembly of the furnace and nozzle equipment every run. The nozzle assembly requires entering the main spray chamber and removing and replacing the nozzle overhead.

The latest design provided a removable basket assembly containing all the essential elements of the spray forming process—the crucible, stopper rod assembly, heaters and all electrical connections, insulation, lid, drop tube with the nozzle attached to the underside which can be removed as a unit for service on the bench by a single technician. Two key features of the removable unit are embedded rod heaters and a air cooling coil. This provides more rapid heat up and cooldown.

In addition, the unit was designed for hydrogen removal from the melt. The multi-step approach involves: 1. Slowly drawing a vacuum after melting. 2. Argon purge through a ¼ in. diameter alumina tube immersed in the molten metal.

1.1.4 Nitrogen Supply System

With the advances in nozzle technology, improvements to the atomizing gas controls in the TAFA vessel were necessary. The main nitrogen system storage capacity and flow rate were increased and new control circuits were added. Specifically, individual vortex shedding mass flow meters were installed on the five nitrogen lines leading the Alcoa III nozzle. In addition, the Nitrogen system was modified to provide atomizing gas for the water test stand directly from the TAFA unit. This substantially increases the gas supply rate for water testing and provides identical instrumentation and control.

1.1.5 Contractor Spray Forming Equipment

INEEL Spray Forming Equipment - described in detail in the Phase I Report [8]. Modifications required for the Alcoa program were enlarging the melt system to 15 lb melt capacity, converting from argon to nitrogen gas and modifications to the nozzle system for scale-up.

MIT Spray Forming Equipment - described in the Phase I Steel Report [8]. Modifications included increasing the crucible and tundish size to a 12 lb capacity. This modification necessitated a new induction coil and power leads.

UCI Spray Chamber - similar in design to the MIT equipment. It was modified to accommodate two large optically flat windows for use with a PDPA.

1.2 Nozzle Development

From an analysis of the spray forming process, three critical objectives of a nozzle system for successful application of spray forming technology to thin sheet production were identified. These are:

1. *Profile of the sprayed deposit.* In order to roll the deposit to the final sheet dimensions without excessive edge cracking the transverse sheet profile must be flat within ±2%.
2. *Deposit porosity.* Studies have shown that it is possible to heal porosity up to 4% during the downstream rolling operation. This porosity must not be interconnected such that oxides will form. Typically, interconnected porosity will occur on the top and bottom surfaces of the deposit while the interior will have closed porosity.
3. *Yield.* The process economics are very sensitive to yield. Yields are lowered due to overspray losses and removal of edge trimmings. In the original proposal, the targets for process yield were determined separately on the basis of 5% overspray and less than 1 in. edge trimming. Both of these requirements are very stringent for any existing nozzle system.

Throughout the program, five different nozzle systems were considered. In addition to the USGA and INEEL nozzles from Phase I, three systems were designed and developed at Alcoa.

1.2.1 Alcoa I Nozzle

Designed by Alcoa's Dr. Ali Ünal, this 4-in. linear nozzle is a confined-liquid gas atomizer based upon a well documented circular design for atomizing powders [2,3] (see Figure 4). Confined liquid nozzles have the advantage of close-coupling the gas and liquid providing for very energy-efficient systems. Unfortunately, one of their main drawbacks is their reduced operating window, due mainly to the complex way in which the operating variables interact. The aerodynamic interactions between the gas jets and the metal delivery tube affect the pressure at the liquid metal exit causing non-free fall metal delivery.

In this linear nozzle design, the gas jets consist of adjustable rectangular slits placed on either side of the confined liquid metal nozzle. It uses a converging/diverging gas jet to achieve a moderately underexpanded supersonic jet at the point of impingement with the metal stream. Replaceable liquid tips are used for quick change-out and variation of liquid slit dimensions.

1.2.2 USGA Nozzle

The USGA nozzle is another typical example of the confined-liquid gas atomizer, in which the metal delivery tube is situated in close proximity to the high velocity gas jets [4]. An integral part of this design is the use of Hartman shock tubes to provide ultrasonic energy to the melt, aiding atomization (see Figure 5). There were major differences from the Phase I program nozzle design—the inclusion of a vaned gas diffuser section to deliver the gas uniformly, use of replaceable front face plates, and the unit was designed to have adjustable settings for the angle of gas impingement and the horizontal and vertical offset of the gas slits relative to the metal pour tip.

In this program two lengths of the USGA nozzle were tested: A 4-in. wide unit whose spray pattern was dominated by end effects, and an 8-in. unit built by coupling two 4-in. units side by side. This assembly initially used 8 in. continuous liquid and gas slits. The graphite metal pour slit was modified to include a small bridge in the center to prevent deflection by the impinging gas jets. The nozzle assembly is shown spraying water in Figure 6. Regardless of width, both the water spray and metal spray profiles retained the same characteristic Gaussian shape.

Several variations on using curtains of gas or aerodynamic shrouds to reshape the spray plume in the vicinity of the substrate were tried using water spray testing. This "homogenizer" is basically a metal shroud with directed gas jets to provide a curtain of gas along the wall of the shroud to contain and direct the spray.

The first attempt was to use an 8 in. diameter Exair® Air Amplifier 4 in. downstream of the pour tube with the spray directed into the throat. Visually, the unit provides a more uniform spray, however, there was significant wetting of the walls even when operated at high pressures. The resultant effect was the gas flow was doubled and the droplets were impacting on the substrate at a very high velocity. This caused significant splashing parallel to the long dimension of the nozzle (perpendicular to the direction of substrate movement).

The second attempt used Exair® Air Knives which use the Coanda effect to produce a linear gas jet. The air knives were positioned at various points along the length of the spray plume to determine their effects. It was found that it was possible to redirect the front and rear edge of the spray into the main body of the spray near the substrate with standard air knives. Closer to the nozzle, however, the air knives mostly disturbed the spray plume by entraining a significant portion of droplets whenever it was moved near enough to the spray plume to change the shape.

A rectangular version of the air knife was constructed. The device measured approximately 6 in. x 8 in. with 0.018 in. gas jets on all four sides. The spray was directed into the center of the jet. By positioning the unit half the distance to the substrate, it was possible to reduce the spreading of the spray plume. However, moving the device closer to the nozzle or operating at too high a pressure created a chimney effect in which the spray droplets were carried opposite the nozzle flow direction. The gas consumption of the rectangular jet was more than twice the atomizing nozzle. This approach was abandoned without further testing.

Another approach which was tried to counter the Gaussian profile of the linear nozzle was to specially contour the liquid delivery slit opening to distribute more metal to the ends of the tip. In simple pour tests with the modified slit, a sheet of water maintained a sheet configuration for a significantly greater distance before surface tension effects collapsed the sheet into a thick stream. In water spray tests, there was no noticeable difference in the spray pattern with the modified slit compared to the standard slit.

These observations supported a theory that the gas dynamics of the atomizing jet create a low pressure region at the tip which is strong enough to redistribute the liquid feed along the nozzle tip. The implication is that the gas dynamics are significantly more important than the liquid feed for controlling the shape of the deposit, an important finding. Following this theory, the focus of nozzle development was shifted to understanding and controlling gas dynamics to achieve better control of the spray profile.

The USGA nozzle did not meet the program objectives for flatness. After extensive review, two approaches were adopted: 1. Concentrate on modifying the USGA spray plume with devices to reshape and confine the spray, and 2. Design a new deposition system. The latter led to the development of the Alcoa II nozzle design.

1.2.3 Alcoa II Nozzle

This linear nozzle design was based on the concept that an extended shroud will confine and control the shape of the spray plume. The atomizing gas jets are used to create a thick gas boundary layer on the sides of the shroud to protect the surface. A schematic of the original design is shown in Figure 7. The amount of entrained gas was controlled by means of vents which, in turn, had a direct effect on the spray pattern.

Features of the Alcoa II nozzle included:

- It is a free fall (un-confined) atomizer. Free fall atomizers have a broader operating window than confined gas atomizers. Also, they are much less prone to freeze up because they do not have a cold gas impinging on the tip.
- Gas entrainment into the spray plume can be controlled, providing better control of droplet cooling.
- The atomizing gas jets are used to create a thick gas boundary layer along the sides of the shroud to protect against droplet sticking.
- The shroud should equalize the mass distribution of the spray to give a uniform profile.

The spray profiles were significantly better than any observed on the previous nozzles. Several problem areas were identified:

- The liquid stream was unstable and would randomly deflect from one side to the other depositing droplets on the gas jet exit. Stabilization required conditioning the liquid flow with a long tapered delivery tip with the exit near to the gas jets.
- During operation, significant reverse flow was observed in the shield area. Changing the angles had little effect on the reverse flow. This caused severe impingement problem with the liquid on the shields which was most prevalent on the side shields. Adding a second set of gas jets at the ends of the nozzle perpendicular to the slit improved this condition by providing a gas curtain on the end shield.

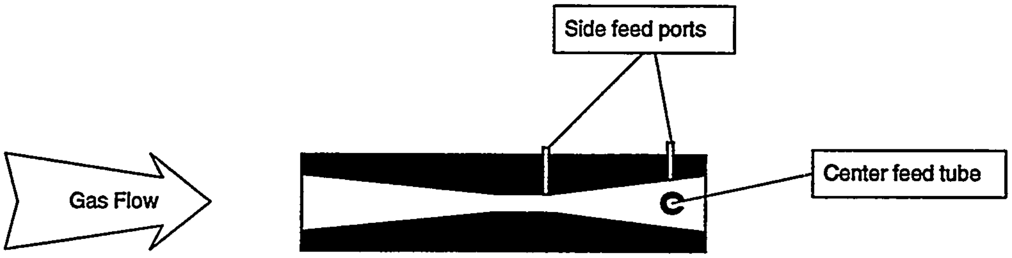
The nozzle was redesigned on the basis of the above tests. The most significant modification was the so called "race track" atomizer in which the slit totally encompasses the metal stream to create a 360° curtain of gas. The shroud was also redesigned to have a constant 7° divergence in all directions. The atomizer unit was machined from steel and the shroud from aluminum so that metal spray trials could be made. A rendering of the nozzle assembly is shown in Figure 8.

Water spray profiles with the Alcoa II nozzle with a 6 in. shroud were vastly superior to any nozzle tested. However, there was still significant liquid impingement inside the shroud. Metal spray tests with the 3 in. shroud were not successful due to metal sticking to the shroud. The deposits had a low solid fraction content indicating that either atomization was poor or there was not enough entrained cooling gas. The nozzle could not be tested at a higher atomizing pressure because limitations to the gas capacity of the TAFA unit.

1.2.4 INEEL Nozzle

The focus of the program at INEEL was to demonstrate the feasibility of using the deLaval linear nozzle system in spray forming aluminum sheet. After early success at producing a flat profile with a 1.3 in. wide nozzle, the emphasis was placed on establishing scale-up principles. Because of equipment limitations at INEEL, the scale-up was limited to 4 in. The critical dimensions used for the scaled up nozzle are shown in Table 3.

Table 3 -- INEEL Nozzle Configurations



Nozzle Version	Inlet Angle	Outlet Angle	Feed Location	Nozzle Width
C1	6	6	Long. Center Feed Tube	0.66"
C2	6	10	Long. Center Feed Tube	1.30"
C3	6	10	Long. Center Feed Tube	2.6"
C4	6	10	Long. Center Feed Tube	4.0"

Scale-up tests to 2.6 in. were carried out at INEEL using their horizontal spray set-up. At Alcoa, the nozzle was adapted to the downward spraying configuration required by the TAFA unit.
A Plexiglas model was constructed for use with water spray tests. These tests immediately showed flow separation was occurring in the transition from the gas supply to the 2.6 in. slot,

extending through the full length of the nozzle. The problem was solved by using a wire mesh to diffuse the high velocity flow from the gas inlet.

Patternator studies were conducted to select among various feed tube configurations. The water spray tests indicated that a split feed tube concept resulted in flatter profiles but none of the profiles were as flat as deposits prepared at INEEL.

The 2.6 in. nozzle was scaled-up to 8 in. for water spray trials and metal spray tests by extending the width of the nozzle bore. The design is shown in Figure 9. The slit dimensions were sized to match the metal delivery per unit nozzle width of the 2.6 in. nozzle. Liquid feed rate with this design an order of magnitude lower than the USGA or Alcoa II nozzles.

Water spray droplets were observed to collect on the walls of the faceplate bore. Most were near the exit but some were upstream of the tubes indicating the presence of undesirable flow separation and backflow. Drilling the holes completely through the tubes seemed to alleviate backflow problems, but at the expense of a substantial reduction of the liquid flow rate.

Metal spray tests in the TAFA unit were conducted with both a 2.6 in. and 8 in. nozzle system. The results with the 2.6 in. nozzle were not as encouraging as observed at INEEL. For the limited number of runs tried at ATC, the spray deposits were either too "wet" or too "dry," with profiles typically Gaussian.

Metal and water spray deposit profiles were not significantly better than the USGA and Alcoa II nozzles. In addition, scale-up of the INEEL nozzle would require significant development especially for the metal feed design system, and the productivity of the nozzle was too low to meet the program's requirements. Increased productivity would require totally re-designing the gas system and metal feed system. Based on this work, development on the INEEL nozzle was terminated.

1.2.5 Alcoa III Nozzle Development

After carefully reviewing the body of nozzle data, literature references, and internal theories on spray profile control, the evidence strongly pointed to the necessity of controlling the atomizing gas dynamics to control the spray. A decision was made to develop a new linear nozzle system which incorporated all of the collective knowledge gained from testing.

We observed that the shape of the gas velocity profile and the water spray mass flux profile were highly correlated. Both exhibited the same trends in spatial distribution as the spray developed downstream. This led to a theory that the shape of spray profile in a linear nozzle is dominated by the gas dynamics of the atomizing jet.

A review of the literature for the free expansion characteristics of 3-D rectangular gas jets [5,6] yielded a good understanding of the effects of gas entrainment on the shape and velocity decay of the jet. The data of Trentecoste and Sforza [5] show that freely expanding linear jets decay to become axisymmetric at some distance downstream. Thus, to maintain a flat deposit profile, the nozzle must be designed to operate on the left hand side of the curve in Figure 10. Therefore the minimum size for testing in the bench scale unit was increased to 8 in. for all subsequent testing.

The Alcoa III, was designed based on the principles discovered throughout this study. It has features of all four of the previous nozzles, while incorporating a special gas control scheme. The Alcoa III linear nozzle system is shown in Figure 11. Figure 12 shows a transverse cutaway. A metal gauze is used inside to distribute flow from the inlet pipes to the gas slits. A key feature of the nozzle is the ability to adjust individual pressures to control the shape of a sprayed deposit. Under normal operating conditions, the nozzle is operated in a symmetric fashion in which pressure settings on the upstream and downstream halves of the nozzle are from a common source, and chamber pressures P1 and P2 are set equal to P5 and P4, respectively (Figure 11).

The converging/diverging geometry of the exit gas slit results in an overexpanded supersonic gas jet at pressures greater than the critical pressure. The nozzle was designed to operate in a relatively low pressure range of 40-80 psi to minimize compressor costs. The nozzle is operated by adjusting the gas to metal ratio (G/M) to control the fraction solid in the spray. The pressures P1 through P5, are adjusted relative to each other to control the shape of the deposit. The protrusion distance and gap are set according to the desired atomizing behavior.

During the development of the original USGA linear nozzle different patterns of holes were used in the metal pour tip [7]. These were eventually replaced by a thin slit in an effort to obtain a flatter profile. With the profile control features of Alcoa III nozzle, it is possible to revert to a series of holes. In addition to easier machining, the larger diameter holes will help prevent plugging with metallic inclusions.

Water spray patternation was used extensively to determine the factors controlling the mass flux profiles of the spray.

Measurements on the short axis spray profile provide information on leading edge and trailing edge effects as well as process effects which are deposition rate sensitive such as mushy layer thickness. Patternator studies show the short axis profile to be typically Gaussian shaped. The spray angle (spray width) and peak height vary according to the protrusion length. There is a rough trend towards a narrower spray as the protrusion length increases.

The long axis spray profile is directly related to the strip profile. The enabling technology of the Alcoa III nozzle is the ability to control the shape of the long axis mass flux profile by locally adjusting the outlet gas dynamics to compensate for the natural tendency of the spray to assume a Gaussian distribution downstream.

Other factors which have been observed to affect the profile adjustments are various combinations of baffles and the type of packing materials in the zones. At low operating pressures there are observable voids in the spray pattern at the location of the baffles. Therefore, we find it necessary to operate without baffles. As the nozzle pressure is increased the range of pressure adjustment is not enough to flatten the spray profile. So it is necessary to use the end baffles. As the pressure is increased further, it is necessary to use all of the baffles and to create separate zones for each gas feed. Overall it was shown that baffle design and the choice of porous packing materials can affect the profile of the deposit.

1.3 Spray Forming Test & Evaluation

There are a large number of geometrical aspects of the various nozzles which affect their operation. A sequence of tests were used to narrow the range of parameters to be tested in actual metal spray tests. This involved a multi-step approach including water spray visualization, dynamic pressure measurements to map the gas flow field, deposition studies with water sprays, deposition studies with metal sprays and additional diagnostics with a PDPA, high speed photography and acoustic measurements.

1.3.1 Spray Visualization

Spray visualization tests with water sprays were particularly useful checking initial setup and observing potential operating problems. Photographic techniques were used to check for spray uniformity and atomization characteristics. Figure 13 illustrates the atomizing phenomena using water as the liquid medium.

1.3.2 High Speed Photography

High speed photographic studies were performed by Prof. Charlie E. Miller, Northpoint Labs, and the Massachusetts Institute of Technology (MIT) in conjunction with Dr. Nick Grant's spray forming program. Using sophisticated photographic equipment, Prof. Miller attempted to image the break up of the liquid metal stream into droplets near the nozzle and the impact of the droplets into the substrate.

Two pieces of equipment were used: a Kodak 4540 high speed video system and the IMACON[1]. Most of the equipment setup was performed during water sprays, with some work on tin and aluminum. Variables included: liquid slit length, camera magnification, and frame rate. An assortment of lighting options were used.

Streak imaging was also attempted to gain insight into the primary particle velocities and the amount of material bouncing off the substrate. With this technique, particles moving in the plane register as line streaks. With some interpretation, particle velocity and direction are determined from the streak angle. The use of a continuous "sheet light" source having a 0.125 in. thickness, passing through the spray plume at right angles to the camera axis provided an improvement over normal streak imaging.

---

[1] Image Converter Camera

1.3.3 Dynamic Pressure Parametric Tests

The main purpose of this work was to provide a means to visualize the spray plume. By looking at the gas-side only, parametric tests were run to find the set of parameters needed which provides the narrowest, most uniform spray distribution. Using 1/16th inch diameter pitot tubes, the dynamic pressure in the spray plume was measured as a function of gas pressure, gas jet angle, and vertical offset. The technique is similar to that reported by Moir and Jones [9]. Figure 14 shows a sample of the output of the test.

1.3.4 Parametric Study of Deposit Profiles

This study was performed in two phases:
1. Deposition studies with water using a patternator.
2. Deposition studies with molten metal.

1.3.4.1 Water Spray Tests

Water spray tests were used to evaluate the effect of nozzle geometry and operating parameter changes on the mass distribution of the spray. These mass flux profiles were done by collecting water in a series of test tubes swept across the top of a substrate at a specified deposition length. Figure 15 shows pictures of the water spray patternator used in this study. By establishing a "flatness" parameter based on the standard deviation of the patternator data over a pre-defined width, we can analyze and compare systems.

1.3.4.2 TAFA Metal Spray Tests

Metal spray tests provide measurable deposits. In addition to reflecting the mass flux profile of the spray, the deposits show other factors such as droplet sticking, splashing, and flattening of the mushy surface by the high pressure atomizing gas. None of these can be quantified with the water patternator. We found that the metal deposit spray profile was sometimes different from the water spray profile because the actual nozzle pressures during the metal spray run did not reproduce those in the water spray despite having the same set pressures. It is believe that this occurs due to the dimensions of the gas slit changing when the nozzle is hot, but we were never able to verify this effect. Despite the differences between water and metal sprays, the profile of the spray measured with the water patternator provided a good approximation of the metal cross-sections produced in the TAFA unit.

It was generally not possible to predict the relative pressures which optimized the profile. Testing was required for each gas flow rate regime (average pressure). However, on the Alcoa III nozzle, for small variations in gas flow rate, we found that we could scale individual chamber pressures according to the ratio of the absolute pressure in each chamber. For the TAFA metal spray tests, settings were matched up to corresponding water spray tests. Slight corrections in flow rate were made holding the ratio of the absolute pressures in the chambers constant.

Metal spray tests were generally done in campaigns to test features of a particular nozzle with a general emphasis on deposit profile. Test conditions would also be set up for secondary purposes, for instance, to provide deposits with a wide range of porosity for rolling studies to determine the amount of deformation required to close pores or to examine the effect of substrate materials and auxiliary gas jets on bottom surface porosity. Attachment II contains a listing of the 82 runs performed under this program. Major process variables considered were: melt superheat, spray distance, substrate, nozzle dependent variables of nozzle pressure gas metal ratio, liquid flow rates, and gas flow rates.

Deposit flatness was measured as the standard deviation of the normalized deposit thickness over a 6.2 in. or 7.6 in. width of the deposit. Thickness measurements are normalized with respect to the deposit cross section so that the sum of the normalized thickness values is unity. This makes the measures independent of actual deposit thickness.

1.3.4.3 Marko Metal Spray Tests

The Marko unit uses a fixed substrate in which a deposit is built up. The process is transient in nature since the deposit thickness and thermal conditions continuously change over the course of the run. The unit has proved useful to determine process conditions prior to committing to a larger scale run in the TAFA unit. Attachment II contains a table noting the 75 runs performed under this program.

The trials showed that pressure, spray distance and melt temperature, have a statistically significant effect on porosity. The Marko unit tests are significant in that they indicate that the optimum conditions for reduced porosity and high yields are short spray distances and lower nozzle pressures. However these conditions produce a type of porosity (small numbers of large pores) that may not be conducive to optimum sheet properties where large pores are typically associated with defects. Like the TAFA unit there is also a possibility that the larger pores may be caused by hydrogen. From a fundamental perspective, the evidence points to the droplet impact velocity as one of the most significant parameters which affects yield and porosity.

The Marko unit was also used to understand various substrate dynamics. The properties of the substrate material are known to affect the thickness of the porous layer next to the substrate. For example, restricting substrate-side heat transfer will minimize bottom porosity. During the research, a series of screening tests were run with variations of the plate/foil/insulating board substrate.

In addition to porosity, an important issue related to the substrate material is its release properties. For a continuous process, the deposit will have to release from the substrate easily leaving the deposit with a uniform surface suitable for rolling. In general, sticking occurs whenever a coating is not used regardless of finish (i.e. bright mill finish, abraded or grit blasted). Graphite spray coatings transferred in significant quantity to the spray deposits. While none of the treatments tested were promising, the results point in the direction of light graphite coatings applied to a bright finish.

1.3.5 Advanced Characterization Techniques

1.3.5.1 Acoustic Tests

The N. Grant design of the Hartman cavity in the USGA nozzle is a significant departure from the Nilsson design [10]. Several sets of tests were run to determine if the USGA nozzle was producing acoustic vibrations in the ultrasonic regime and whether there was a difference in the atomization behavior with and without the Hartman shock devices.

A set of acoustic measurements were made using a high frequency microphone located approximately 1 in. from the exit of the gas slits. The output from the microphone was analyzed using a power spectrum analyzer to determine the intensity and frequency of characteristic vibrations. Based on these very simple tests, we concluded that the Hartman devices are not providing significant acoustic energy.

Additional Schlieren and shadowgraph comparisons were conducted at CMU to determine the effectiveness of the Hartman devices. These tests also found that the Hartman cavity had little effect on the droplet sizes or spray development in the pressure range of interest. We concluded that the Hartman devices were not worth pursuing further for this application.

1.3.5.2 Phase Doppler Particle Analyzer (PDPA)

The PDPA was used to determine the distribution of droplet sizes and droplet velocity in the spray. This data is useful to verify spray models as well as to enhance understanding of a particular nozzle system and to insure that there are no peculiarities for a given nozzle arrangement.

PDPA studies were carried out at Alcoa, CMU and UCI. The PDPA program at CMU focused on the effect of gas pressure on the droplet velocity and size using water sprays with the USGA-1 nozzle. The University of California - Irvine studies focused on establishing correlation between water spray and metal spray test data with the same nozzle. This information allows us to perform more nozzle tests with water thereby decreasing the development time for evaluating nozzle design and operating changes.

Detailed studies were conducted at CMU in which the effect of pressure was also examined. There is an apparent limit to the effectiveness of increasing gas pressure beyond which additional pressure produces little decrease in droplet size. The spatial distribution of the drop size and velocity were measured for the long axis and short axis. Along the short axis, larger droplets have a low velocity at the outer edges of the spray indicating that they are escaping the high velocity gas field. This has implications for the leading and trailing edges of the spray, the low mass flux of large droplets combined with long flight times (low velocity) of the leading edge will lead to a condition which will promote considerable substrate side porosity.

1.3.5.3 Enthalpy Probe

Another important aspect of the droplets is the thermal state. Since, in the spray forming process, the metal droplets are cooled as they are conveyed to the substrate by the atomizing gas, the extent of cooling is dependent on the particle and gas velocity, the particle size, and the time of flight. Depending on the thermal history, the impacting droplets will arrive at the substrate in either a fully solid, fully liquid or semi-solid state. Under the proper conditions, the mixture of droplets will consolidate to form a thin mushy or semi-solid deposit on the top surface of the spray formed deposit. This layer solidifies incrementally as heat is transferred into the substrate. The thickness and average solid fraction of the mushy layer are important parameters which have been strongly correlated to the porosity and microstructure of the deposit. Unfortunately, neither quantity can be measured directly.

During this project a probe was developed to measure the enthalpy of the impacting metal droplets. The enthalpy data can be used to indirectly determine the solid fraction of the impacting droplets. The probe uses a calorimetric technique in which the temperature rise in a thermally isolated copper disc is measured during the deposition of a thin sprayed deposit. After correcting for heat losses to the surroundings, the heat content or enthalpy of the sprayed deposit can be determined. The solid fraction of impacting droplets is computed from a temperature estimated from enthalpy and phase diagram relationship of the aluminum alloy.

The probe has been used to verify and update our computer models of the spray forming process. Thus the thermal history and process conditions can be correlated to microstructural features such as grain size and porosity.

1.3.6 Electromagnetic / Electrostatic Plume Control

One option considered for shaping the plume and controlling the deposition profile is to use electrostatic and/or electromagnetic forces. Calculations were performed to examine the feasibility of both of these options.

For the electromagnetic case, the forces on liquid aluminum droplets of various sizes in an AC electromagnetic gradient field were computed and compared to hydrodynamic forces from gas atomization. The following considerations are noted: (1) The force is proportional and in the opposite direction to the gradient of the magnetic field. To provide a large force, coils should be designed to provide a high field gradient. The force will be directed away from the coils and will tend to keep droplets away from the coils. (2) The phase of the AC circulating current must be considered because only the component in-phase with the applied magnetic field is effective in generating a net force on the droplet, integrated over the entire cycle. (3) The force is proportional to the field strength multiplied by the field gradient. Therefore, it depends very strongly on the radius of the droplet and the frequency of the field.

Three assumptions were made to perform the calculations: (1) The spherical drop was represented as a cylindrical bead having a hollow space along its axis. (2) To calculate the electrical resistance of current flow around the bead, all of the metal in the drop was considered to be disposed on the cylindrical shell of the bead. (3) To estimate the magnetic energy associated with the current flowing around the bead, it was assumed that the magnetic field exists on the inside of the bead, and thus it behaves like a solenoid. These approximations may introduce errors in the calculation in the force which may be off by a factor of two. The calculations are nevertheless useful because they show the enormous variation in the force due to the droplet radius and AC induction coil frequency and field strength.

In addition to the force on the droplet, the stokes velocity was computed. This is the relative velocity perpendicular to the direction of flow. It is very useful to compare this number with the droplet velocities created by the atomization gas (on the order of 60 m/s). The maximum horizontal droplet velocity produced by an induction field is many orders of magnitude less than the vertical droplet velocity.

A similar analysis for electrostatics indicated that only droplets <10μ could be displaced in an electric field. No further work on electromagnetics or electrostatics is planned.

1.3.7 Laser Stripes

Following INEEL developments in Phase I, a laser stripe device was tried. Basically, a line shaped laser beam with nearly uniform intensity is projected across the width of the deposit at an angle. A video camera records the shape of the projected line above the deposit. At a 45 degree angle, the displacement of the line image from the substrate is the same as the deposit thickness. A solid state laser system from LASERIS corporation was used for the trials.

1.4 Computer Modeling

The objective of the modeling work was to establish an analysis capability for the Spray Forming Project to fortify our knowledge and help design and control the process. The Alcoa models basically extended established modeling tools to include additional features for more rigorous fit-for-purpose simulations of the spray forming process. Figure 16 shows the five zones of the process targeted by mathematical models: atomization, chamber, spray, deposition, and process, respectively. Also noted are the critical process information that models are designed to compute. Following are the simulation requirements and approaches taken for each zone:

Atomization - Most atomization models are empirically based, therefore, this task relies exclusively on experimental data provided by CMU, UCI and Alcoa. Characterization should include droplet (particle) size distribution (PSD), and mass distribution (MD), as functions of atomization conditions such as gas-to-metal ratio (G/M). Computational fluid dynamics models can be used to calculate the gas flow condition within and around the nozzle. The condition of the gas critically influences droplet break-up as well as the droplet cooling ability of the gas.

Chamber and Spray - For the chamber and spray simulations we would like to develop a full-scale three-dimensional spray model that will address the effects from chamber geometry, gas-droplet interaction and droplet-droplet interaction simultaneously. But due to the complex nature of the problem, we used an alternate approach:

Chamber — First, we developed a two-dimensional model which solves simultaneously for the gas flow fields and the droplet trajectories for various droplet size distributions as a result of atomization. The droplet motion and the gas flow field are coupled. At this stage, the droplet thermal history is not solved for due to the complexity in treating the droplet solidification problem. We use the 2-D results to derive correlation for the gas entrainment that will then be used for a one-dimensional spray model for the spray simulation. Chamber model results can also be used to recommend appropriate chamber designs to minimize the magnitude of overspray.

Spray — Second, a one-dimensional transport model simulating the heat and momentum transfer of gas and droplet during spray is developed. The model predicts the fraction of solid of the droplet as it arrives at the substrate. It also predicts velocities and thermal histories of both gas and droplets during the spray. Information obtained from the 2-D chamber model is used to characterize the gas.

Effectively we have a quasi-two-dimensional methodology to model the transport phenomena in the chamber and spray.

Metal Deposit - The conditions of droplets arriving at the substrate predicted by the above chamber and spray models are used as the input to the deposition model for metal deposit calculations. The deposition model predicts deposit profile and temperature. Sticking phenomenon and porosity formation as a result of deposition process are not treated because they are difficult to model.

Process - With the establishment of chamber, spray and deposition models, we can then study the spray forming process as a whole so that the effect of process input conditions such as alloy, superheat and gas to metal ratio to the product condition can be quantified. Using the model, we can predict and optimize the total yield as well as product quality given the process input conditions. We can also develop simplified process equations that are fitted for control/monitoring scheme implementation.

Modeling the spray forming process has attracted increasing attention in recent years. A few examples of the work reported in the literature has been enclosed in Attachment III.

1.4.1 Osprey Computational Models

Through a license agreement with the Osprey Metals Ltd., we have obtained the computer codes developed by Osprey for simulating the of spray forming process. The Osprey models are composed of the following four separate modules:

- Spray Module — This is a one-dimensional model which predicts the velocities, temperatures, and fractions of solid of droplets at various sizes under pre-specified mass and size distributions. It also determines the average fraction of solid of the sprayed metal as well as the gas temperature and velocity.

- Linear Module — This module calculates the resultant mass profile and the enthalpy of the sprayed metal as received by the moving substrate. Such information is required for the subsequent deposition calculation. The input to this module comes from (1) results from the Spray module, (2) specifications of the substrate conditions, (3) overspray characterization, and (4) mass profile of droplets in the spray zone.
- Plate Module — This module calculates the one-dimensional through-thickness temperature distribution as well as the deposition profile in the casting direction. Solutions are also plotted graphically on the computer screen.
- Chamber Module — This module performs an overall energy balance for the spray system. It estimates the thermal transient of the spray chamber. Such information is useful for the chamber design to minimize the thermal instability of the chamber particularly during the start-up or interrupting periods.

1.4.2 Alcoa Computational Approach

An alternate approach to the Osprey model was undertaken in which a 3-dimensional model was developed in collaboration with Prof. M-K Chyu at CMU. The model simultaneously solves the multiphase turbulent transport equations for convective transport of metal droplets, heat transfer in flight, droplet solidification including recalescence and predicts the deposit shape and temperature distribution. The numerical procedure employed is a fully interactive combination of Eulerian flow and Lagrangian droplet calculations.

Droplet dispersion by turbulent fluctuation is modeled based on droplet interaction with successive eddies and a Monte Carlo method. Turbulence is modeled by a k-e model. A five-stage aluminum solidification process is used: convective cooling, nucleation and recalescence, segregated solidification, eutectic solidification, and cooling in the solid state. The droplet-substrate interaction, which determines over-spray, deposition quality, and process efficiency, was described based on the Weber Number and Thin Shell Theory.

Statistical results obtained from this model reveal important information on the droplet distribution velocity, temperature, solidification, and droplet shape. The model can be used to examine the effects of chamber geometry, including the use of baffles and air knives, on the spray transport as well as the deposit shape and quality. Results obtained from the study showed favorable agreement with the available test data.

The spray simulation code was modified to deliver the capability to address the needs for ADU development work as well as the water spray experiments. Specifically:

- Modifying the chamber shape from a cylindrical shape to that most likely to be used in the final ADU design.
- Adding user friendly features for running the code, particularly on shape and meshes.

Simulation results on the deposit profile from water spray in a simplified rectangular chamber are as shown in Figures 17 and 18. Figure 17 shows a normalized three-dimensional deposit profile distribution on a fixed flat substrate. Figure 18 shows the effect of reducing chamber size. The preform shape is an accumulated result based on about 10,000 sampled computational droplets.

A nozzle gas dynamics model was jointly developed with Professor T. I. Shih (originally at CMU, now at Michigan State University) in order to better understand and quantify the gas dynamics in the nozzle. This provided a method to optimize the nozzle design and performance. Computed results showed that there is supersonic flow in the nozzle throat area. Shock waves are also clearly captured by the model.

Both the nozzle throat dimension and the inlet gas pressure are important variables that determine the resultant gas flow condition as the gas exits the nozzle.

1.4.3 Deposit Thermal Model for Marko Spray Unit

It is generally believed that the liquid fraction of the metal spray arriving at the deposit is controlling the level of porosity.

A two-dimensional transient thermal model was developed to simulate the thermal history of a deposit as a result of the spray profile in the Marko unit. The model is a useful tool to study the influence of process parameters on the formation of base (substrate-side) and bulk porosity. The model was used to assist the design of experiments to find the operating windows for minimizing porosity in the bulk.

1.5 Product Development

Spray formed deposits were prepared in the Marko mini-spray chamber. In addition to the binary alloys, this unit has been used to spray 3003, 6061, 6009 and 6111.

1.5.1 Binary Alloy Study

The binary alloy studies focused on improving our overall understanding of the spray forming process such that benefits can be effectively used in a commercial product. The Al-Cu (eutectic) and Al-Zr (peritectic) binary systems were selected as model alloys because each has been well characterized by others in the literature.

The Al-Cu alloy forms Al-CuAl$_2$ near the aluminum-rich corner of the phase diagram. The eutectic concentration is at 5.65% Cu. There is a well established relationship between secondary arm spacing and cooling rate [11]. Thus using quantitative metallographic techniques, the cooling rate can be established for individual particles. This approach was applied at MIT to study the cooling rate and undercooling behavior of droplets. MIT showed the undercooling of droplets is strongly affected by the alloying elements. Studies showed that Al-Fe binary alloys were more significantly prone to undercool than the Al-Cu alloy.

The Al-Zr alloy system was selected because Zr forms fine dispersoids which are very effective in controlling recrystallization and grain growth in commercial aluminum alloys. Since spray forming has a high initial rate of cooling, more Zr is expected to be retained in solid solution in spray formed material than in an ingot metallurgy alloy. For conventional ingot metallurgy alloys, additions of Zr are limited to equilibrium concentration of 0.11%. Although higher concentrations are desirable, they result in the formation of coarse Al_3Zr needles during slow cooling through the $L+Al_3Zr$ phase field. In spray forming, the high cooling rate should result in a supersaturated solid solution of zirconium in aluminum. During subsequent thermo-mechanical processing, desirable, fine Al_3Zr intermetallics will then precipitate.

Spray trials were run to determine the maximum additions of Zr which can be made without the formation of coarse Al_3Zr. Binary alloys with Zr concentration varying from 0.1 to 2.0% Zr were to be spray formed in the Marko spray forming unit. No Al_3Zr precipitates were observed up to 0.529% Zr. Higher concentrations were not tried because of temperature limitations on the melting equipment. These results are significant because they demonstrate that the solidification path created by the spray forming process can retain Zr in solution at levels several times its equilibrium concentration.

1.6 Deposit Characterization of Commercial Alloys

Studies were carried out at Alcoa, MIT, and INEEL. The Alcoa studies deal with porosity development, microstructural development, effect of porosity and rolling conditions on properties, and development of constitutive relationships and rolling process models for optimizing downstream processing conditions (hot and cold rolling, heat treating, annealing, etc.).

Figure 19 shows a typical microstucture for Alloy 3003 at three different locations: 19a was taken from the region close to the top of the deposit. The grain structure in this region is equiaxed and the grain size is less than 60 µm. The pores in this region are more or less isolated and tend to be spherical in shape; 19b is a micrograph taken from the middle section of the deposit. The grain structure in this region is also equiaxed. The pores in this region are comparable with the rest of the deposit.; 19c was taken from a location adjacent to the bottom of the deposit. The structure in this region is very porous. The porosity is irregular in shape. The pores could be as large as 2000 µm in size and are often interconnected to each other.

The porosity in the bottom of the deposit will be referred to as "substrate-side porosity" and the porosity in the rest of the deposit will be referred to as "bulk porosity." Also, the measured thickness of the substrate-side porosity layer is used to represent the degree of severity of the porosity in this region. It is believed that the substrate-side porosity forms as a result of the combined effects of chilling by the substrate and a low mass/heat flux in the leading edge during deposition. In this layer, the solidification rate is much higher than the deposition rate. The splats form from those droplets that are still in liquid form on impact. The completely solidified droplets in this substrate-side porosity layer could come either from the leading edge of the spray or from the entrained gas developed during spray forming. The substrate-side porosity of a deposit is strongly affected by the thermal properties of the substrate, substrate temperature and spray distance.

The observed size of the bulk pores ranges from 20 to 500 microns. Unlike the substrate-side porosity, the morphology of the bulk pores is either equiaxed or spherical in shape. It appears that the volume fraction and the size of the pores in the bulk is a strong function of the distance from the bottom the deposit. Judging from the morphology of the pores, it is quite clear that formation mechanism for bulk porosity is very different from that for base porosity. The formation mechanism for bulk porosity will be discussed in a later section. The size and the distribution of pores in the bulk are strongly dependent on the spray conditions.

For a given atomization condition, substrate-side porosity is related to the liquid content of the leading edge of the spray plume and to the heat flux to the substrate. The spray distance strongly affects the liquid content of the plume, whereas the substrate temperature affects the deposit's cooling rate. In-flight residence time of droplet is shortened with decreasing spray distance and thus the droplets arrive at the substrate with a higher liquid content.

However, pore size is larger in materials deposited on a hot substrate. Such variation in pore size could be the result of coalescence of entrapped N_2 gas pockets in highly liquid regions of the deposit under the influence of droplet impact and buoyancy forces. The middle region of the deposit is formed by core region of the plume which contains droplets with higher liquid content and/or at higher temperatures compared to those at the trailing and leading edges of the plume.

Therefore, an optimum spray distance and substrate temperature regime exist for the elimination of substrate porosity for a given set of atomization conditions. Higher gas pressure results in a decrease in mean particle size with a corresponding increase in cooling rate, finer spray and colder droplets [12].

Droplets bouncing and splashing ahead of the main spray plume affect substrate side porosity which creates a porous "pre-deposit". Two approaches are needed. One is to develop an understanding of how to eliminate droplet bouncing and splashing. The second is to develop a means of redirecting or continuously removing the splashing droplets.

According to results obtained from Guinier X-ray analysis and electron probe analysis, 3003 deposits contains two types of constituent phase: $Al_{12}(Fe,Mn)_3Si$ and $Al_6(Fe,Mn)$. The size of $Al_{12}(Fe,Mn)_3Si$ constituent particles is of the order of a few microns while the $Al_6(Fe,Mn)$ particles are of the order of submicrons in size. The $Al_{12}(Fe,Mn)_3Si$ particles are located along the grain boundaries through the thickness of the deposit. On the other hand, the $Al_6(Fe,Mn)$ particles are normally observed at the center of grains. These $Al_6(Fe,Mn)$ particles can only be found in the region adjacent to the base porosity layer of the deposit. It is believed that these $Al_6(Fe,Mn)$ particles formed originally in flight and were retained in the pre-solidified region during deposition. In the top half of the deposit, these fine particles are absent as a result of remelting. As to the $Al_{12}(Fe,Mn)_3Si$ constituent particles, their size increases with distance from the bottom of the deposit.

Except for the base porosity layer, the microstructure of a deposit consists of equiaxed grains. The size of the grains range from 10 to 40 µm and increases with distance from the bottom of the deposit. It is estimated that the atomized droplets solidified during flight at cooling rates ranging approximately from 10^3 to 10^4 °C/s, depending on the droplet size. Under current spray conditions, cooling rate of a deposit decreases approximately from 60°C/s to 0.6°C/s with distance from the bottom.

During spray forming, the semi-solid slurry in the mushy layer is continuously sheared and vigorously agitated, as in rheocasting, by the high speed gas jet and the arrival of numerous droplets. As a result, the solid particle morphology becomes spheroidal. Based on the measured Mn concentration profiles, it is evident that the spheroidal particles in the mushy layer evolved from dendrites carried into the deposit, and are the precursors to the equiaxed grains in the deposit.

1.7 Thermo-Mechanical Processing

The thermo-mechanical studies included in this project were aimed at developing a rolling practice to produce sheet with the desired characteristics. They also defined characteristics of the as-sprayed deposits needed to achieve the commercially viable sheet products. One of the objectives of the rolling trials was to determine the maximum level of porosity in the as-sprayed deposit which will still produce quality sheet. Bulk porosity typically takes two forms -- "Dry" porosity consisting of small (< 10 µm) irregular pores located at grain boundaries, and "Wet" porosity consisting of larger (> 20 µm) spherically shaped pores randomly distributed throughout the deposit. Typically these pores are nitrogen filled. Figures 20 through 23 are typical photomicrographs of alloy 6111 showing the as-sprayed porosity for deposits representative of low porosity-small pore wet spray, low porosity-large pore wet spray, and high porosity-dry spray.

1.7.1 Sample Prep

The typical process path for the production of sheet begins with hot rolling ingot to an intermediate gage. In some instances the hot rolled intermediate gage is annealed before cold rolling. After cold rolling to final gage, the sheet is coiled and sent to a continuous temper line for heat treating.

Rapid heating to the rolling temperature is desired to simulate commercial spray forming conditions in which deposits are rolled immediately after solidification and to minimize dissolution and precipitation of soluble second phase particles. Infrared heating was, therefore, selected instead of air furnace heating.

On a commercial scale, spray formed deposits will be hot rolled immediately after spray forming and coiled while still hot. To simulate the slow cooling that will occur on the production scale, most of the bench-scale hot rolled deposits were given a simulated coil cool before the next process step (cold roll or anneal plus cold roll). In addition, under production conditions, coiled sheet is usually solution heat treated[2] in a continuous heat treating line where it is uncoiled, passed through an inline heat treating furnace, quenched and recoiled. The line speed is determined by the time required for dissolution. A solution heat treat study was performed to evaluate the influence of rolling conditions and hot line gage anneal on dissolution time. Electrical conductivity provides a semi-quantitative measure of how much solid has gone into solution.

Following cold rolling the samples were solution heat treated. Samples for W-temper metallographic evaluation were heated and cold water quenched. To reveal features of porosity, inclusions, dispersoids and grain structure, samples were evaluated in the as-polished condition, after etching with 0.5% HF and, under polarized light, after electro etching.

1.7.2 Rolling and Heat Treating

1.7.2.1 Alloy 3003

Samples were hot rolled at 19-30% reduction per pass to a final thickness. Typical total deformation was 66% to 75%. The entry temperature was 950°F, the exit temperature was as low as 182°F. The samples were reheated and soaked after every two passes.

Prior to cold rolling, material was annealed and furnace cooled to 450°F, then allowed to cool in air. Materials were cold rolled to approximately H14 and H16 condition.

1.7.2.2 Alloy 6111

The as-sprayed 6111 deposits produced in the TAFA unit under normal spray conditions, typically, have fine equiaxed grains. The grain size ranges from 10 to 50 μm. This grain size is much finer than that normally observed in conventionally cast 6111 alloy ingot (400 μm). The spray deposits are relatively dense compared with typical 3003 spray deposits sprayed earlier in the DoE program. As with 3003, two types of porosity were observed. Base porosity at the substrate-deposit interface typically has a thickness of about 3 mm. The bulk porosity varies depending on the spray conditions.

Samples of the hot rolled plate were electro etched and viewed using polarized light to reveal the grain structure. Representative photomicrographs are shown in Figures 24 and 25. The annealed samples (Figure 26) are fully recrystallized with a grain size of 20-150 μm. The effect of hot roll reduction on final grain size appears to be negligible regardless of the anneal step. The use of the anneal between hot and cold rolling has a much larger effect.

In summary, to achieve a fine grain size when no anneal is used a cold rolling reduction of at least 35% is required. To achieve a similar fine grain when an anneal is used, a cold rolling reduction of 77% is needed. No effect of hot roll reduction on final grain size was observed.

---

[2] Solution heat treating is performed to put all the solute into solid-solution.

When metal is deformed by rolling or other processes, grains acquire a preferred orientation or texture. Often, several ideal orientations coexist. This mix of orientation distributions describes the deformation texture. When the metal is heated, as in annealing or solution heat treating, the material can acquire a new texture.

X-ray diffraction was used to measure the texture of 6111 sheet produced under various treatments. For 6111 produced via ingot metallurgy (I/M), an intermediate anneal is needs to be used to significantly reduced the intensity of the Goss texture. In contrast, the anneal between hot and cold rolling appears to be optional when spray formed starting stock is used. This can result in production cost savings.

Another important result is the influence of the amount of cold rolling on texture. There does not appear to be a systematic change in texture with amount of cold work. Thus from a texture standpoint, any amount of cold work can be used in the design of a processing path for 6111 sheet from spray formed deposits. Overall the samples exhibit a very weak texture, something that is desired for most forming operations.

1.8 Physical/Mechanical Evaluations

Samples were analyzed using optical and electron microscopy techniques in as-sprayed, hot rolled, cold rolled and annealed conditions to track the evolution of properties.

1.8.1 Alloy 3003

Figure 27 shows the overall cross-section of the hot rolled 3003 alloy sample. The porous and splat type microstructure is not healed by rolling.

Longitudinal tensile properties were determined for annealed, H14 and H16 conditions. The results of these tests are given in Table 4. Mechanical properties of Ingot Metallurgy (I/M) 3003 alloy are also included in the table for comparison.

For the annealed condition the strength of the spray formed (S/F) alloy is significantly higher than those of the I/M alloy. For the H14 and H16 conditions, the strength of the S/F alloy is comparable to the I/M alloy. The ductility of the I/M alloy is consistently higher than the S/F material, irrespective of temper condition. It is believed that the presence of layered type microstructure resulting from the presolidified droplets and splat structure adversely affected the ductility of the S/F alloy.

Table 4 - Tensile Properties of 3003 Alloy Deposits from Run 70

	Yield Strength (ksi)	Tensile Strength (ksi)	Elongation (%)
S/F 3003 Annealed	8.7 / 9.2 8.2 / 8.2 8.5 / 9.3	17.1 / 16.9 17.3 / 17.1 17.1 / 16.6	22 / 26 26 / 26 24 / 20
I/M 3003 Annealed	5.8	16	30
S/F 3003-H14	22.2 22.4 21.9	23.4 23.3 23.5	5* 6 5*
I/M 3003-H14	21.0	21.8	8
S/F 3003-H16	27.9 27.0 27.1	28.9 28.5 28.2	5 6 6
I/M 3003-H18	26.8	29.09	4

*Failed outside middle half of gage length.
S/F - 1 in. gage length
I/M - 2 in. gage length

1.8.2 Alloy 6111

Samples of hot rolled sheet were examined to determine the distribution of second phase particles and look for the presence of porosity and inclusions. The hot rolled samples were given a simulated coil cool (see Figure 28). Selected samples were also given a full anneal. Figure 28 shows second phase particles to be fine and uniformly distributed in both annealed and unannealed samples. The majority of the constituent particles are smaller than 5 µm. In contrast, constituent particle size in typical ingot is 10-20 µm. Precipitate particles containing Mg and Si are also very fine; less that 1 µm. These particles may have coarsened slightly during the anneal as is expected.

Sheet samples were aged to the T4 temper by solution heat treating and natural aging for at least 10 days. Samples were aged to T6 temper by artificially aging. To obtain T8 properties, samples were stretched 2% and then artificially aged. Uniaxial tensile properties were measured in three orientations and are listed in Tables 5 and 6.

Table 5 -- Tensile Properties of 6111 Al Alloy (T4, T6, T8)

			Tensile Yield Stress (ksi)			Ultimate Tensile Stress (ksi)			Elongation (%)		
Sample #	Thickness	Temper	L	LT	45	L	LT	45	L	LT	45
739767-1	0.0391	T4	26.1	24.6	25.1	47.3	45.8	45.9	22.5	26	26
739767-2	0.0391	T6	51.8	48.4	48.4	57.5	55.3	55	10	13	13
		T8	44	39.3	39.8	53.9	51.1	51.6	18	18	19
739767-3	0.0385	T4	27	25	25.3	48.4	45.8	45.3	21	20	25
739765-1	0.0825	T4	26.4	25.3	25.2	48.3	47	46.8	25	270	27
739765-2		T4	25.1	25.4	24.9				26	24	26
739765-3	0.0381	T4	27.1	25.1	25	49.2	46.9	46.5	22	26	26
		T8	43.6	38.1	39.3	54.3	51.2	51.1	18	18	18
739815-1	0.0382	T4	23.9	22.3	21.6	44.3	41.5	39.1	24	23	23
		T8	42.7	37.6	36.9	51.6	48.9	48.1	16.5	19	20

Table 6 -- 6111-T4 Sheet Mechanical Properties from ATC Deposits

		Tensile Yield Stress (ksi)			Ultimate Tensile Stress (ksi)			Elongation (%)		
Sample #	Thickness	L	LT	45	L	LT	45	L	LT	45
739862	0.07	24.3	23	23.1	44.5	43.1	43.2	26	28	27
739863-1	0.07	24.8	24.1	23.8	44.6	43.6	43.7	26	24.3	27.8
739863-2	0.036	27.5	25	25.1	47.3	44.5	44.4	24.8	27.8	27
739864	0.036	25.5	23.6	23.6	45.7	43.4	43.1	24.5	25.8	26.8

Typical UTS, TYS and Elongation values for I/M 6111-T4 sheet are 39-44 ksi, 22-25 ksi, and 22-26%. Most of the spray form sheet produced for this study are within or above this range.

1.8.3 Hydraulic Bulge and Forming Limit Diagrams

The hydraulic bulge test provides a measure of a material's formability in biaxial tension and an indication of fracture resistance. Selected sheet samples from rolling trial were tested. In addition, the longitudinal strain hardening behavior determined in uniaxial tension along with the crystallographic texture measurements can be used to predict the forming limit diagram (FLD) for the spray formed material.

Figure 29 shows that the spray formed materials generally possess better strain hardening abilities than I/M 6111. In addition, the predicted FLD for spray formed 6111 are more isotropic than that calculated for an I/M sample.

2.0 ADVANCED DEVELOPMENT UNIT DESIGN AND CONSTRUCTION

Based on our experiences with the TAFA vessel, we believed that it would not be technically prudent to directly scale up from 8 in. to a 24 in. wide pilot plant. We developed a concept in which the scale-up operations would take place in stages, with each stage focusing on closing commercialization technology gaps using a specialized spray unit designed to specifically test each concept in sequence. This Advanced Development Unit (ADU) would be initially much smaller than the Pilot Plant but could be scaled to nearly the same size as the Pilot Plant as process development proceeds.

The ADU unit would be designed to operate both in an experimental mode and in a semi-production mode replacing the Pilot Plant and augmenting the existing TAFA bench unit. The ADU would use modular construction techniques in which prototype modules can be easily attached to the basic spray chamber to test design concepts. Separate modules would be developed for the metal and gas delivery system, nozzle system, spray chamber, shrouding and overspray and cooling gas handling, and substrate system. The modules would be modifiable separately so that future plant concepts can be evaluated effectively.

2.1 Specifications

Alcoa established concepts for the design and construction of the ADU. The unit would be designed to operate both in an experimental mode and in a semi-production mode. The unit would be both scalable and readily modifiable. Given the program's funding level, some of the functions essential for commercialization of the process would not have been included in the ADU. For instance, the ADU would use a flat substrate. This eliminated the engineering development of a belt substrate system, a sheet run out system, and gas seals—items which were likely to very costly but for which there are known engineering solutions. With a flat substrate sheets could be produced sufficiently large that products approximating commercial size sheet could be rolled. Modular construction techniques would be used so that prototype modules could be easily attached. Separate modules would be developed for the metal delivery, atomization nozzle, spray chamber, substrate, gas delivery, gas cleaning/cooling, overspray, and process control system. The modules would be modifiable separately so that future plant concepts could be evaluated effectively.

Some preliminary functional specifications for each module are listed below:

- Melt Delivery Module: The metal delivery module should consist of a separate melter/holder furnace discharging into a tundish with a slot-type discharge port(s) suitable for supplying metal to the linear atomizing nozzle. Commercially available vessels and control systems would be preferred. Feedback control of metal level and metal flow would be provided. The range of metal delivery rates and the accuracy of control system should be specified.
- Nozzle Module: The nozzle module would be based on the Alcoa III nozzle design. Emphasis will be put on a robust design which can be easily maintained and modified.

- Spray Chamber: Modeling work has shown that the chamber shape is tightly coupled to the gas flow patterns and the resultant deposit shape. The approach to be taken should be to design the chamber shape based on the gas flow dynamics and later test these designs using a physical model. A modular spray chamber should be designed that addresses all operational safety aspects of spray forming including air ingress, ignition sources, and geometries which minimize turbulence and pockets of recirculating gas that could result in hot spots in the chamber shell or areas which accumulate overspray powder. Explosion relief panels should be provided to minimize peak pressures should an explosion of overspray powders occur. A pneumatic chamber cleaning system would be designed to clean residual overspray powder prior to opening unit and to replace the manual cleaning operations used in the bench-scale unit. Chamber inserts would be used to optimize the internal chamber design for gas flow. Advanced computer controls and data acquisition methods would be used.
- Substrate Modules: The substrate would initially consist of a moving flat plate. The substrate material could be changed as needed to evaluate commercial substrate materials, coatings, and cooling methods. Provisions would be made to heat and/or cool the substrate. With the flat plate substrate, no metal exit would be provided initially so that the chamber may be kept sealed during a run.
- Gas Delivery System: A high pressure (150 psig) gas supply is required for the nozzle system. Low pressure gas supplies are required for the chamber purge, cooling gas for the shrouds, and to provide make-up gas for leakage through seals. For a commercial operation, it would probably be economical to cool, recycle, and re-compress the process gas. Recycling was not to be included in the Advanced Development Unit design. The exhaust flow should be controlled to maintain a constant static pressure inside the chamber slightly higher than atmospheric, decreasing the likelihood that oxygen from the atmosphere will contaminate the chamber. It is important for both safety and product quality that the oxygen content in the chamber be controlled. Appropriate instrumentation and controls should be provided to interface with the process control computer
- Gas Cleaning Module: The module would be designed to ensure that exhaust gases from the ADU will be adequately cleaned of aluminum overspray particulates before being discharged to the atmosphere. Cyclones and conventional filters are envisioned for the commercial unit. Environmental criteria, capital investment requirements, and operating costs should be estimated. The selection of an appropriate commercial cleaning system should be based on operating data.
- Process Control System: The ADU would be instrumented to monitor and control critical process parameters, such as atomizing and cooling gas flow rates, metal level, metal flow rate, molten metal temperature, temperatures of the substrate at the point of deposition and along the length, substrate speed, gas inlet and exit temperatures, oxygen concentration, and deposit profile.

2.2 Safety

An objective of the Spray Forming of Aluminum Project was the proper resolution of all safety, health and environmental issues. Alcoa conducted a Risk Assessment/Fault-Tree Analysis (RAFT) to determine the potential for fatalities in the spray forming operation, a Project Safety and Health Review (PSHR) which identifies safety, health and environmental issues, and developed Safe Operating Procedures (SOP) for the TAFA (bench scale) and Marko (small scale) units. In addition, the operation was inspected for compliance with Alcoa Mandatory Standards on molten metal and powder safety.

2.2.1 Risk Assessment/Fault-Tree Analysis (RAFT)

In a RAFT the logical combinations of processes and operating failures required to cause major equipment damage leading to personnel injuries/fatalities are determined. The assessment on the Alcoa Spray Forming Unit was performed by Dr. Gary J. Powers, Vice President of Design Sciences, Inc. in 1993 May.

The study showed that, for the equipment and procedures then in place (called the Base Case), the fatality event rate was one in 3,860 years. The RAFT identified six recommendations that would give a Proposed Case fatality event rate of one in 53,900 years. All the recommendations were implemented.

2.2.2 Project Safety and Health Review (PSHR)

The PSHR is a proactive approach to identify and eliminate hazards before the process or project begins or before technology is transferred to Alcoa customers. By bringing together selected persons to review the scope of the process and through discussion and review of a standard PSHR Hazards Questionnaire, hazards and potential hazards are identified, documented and corrective action assigned.

The PSHR identified equipment and procedures needed to insure the safe operation of the units. Again, per Alcoa guidelines, all items were implemented.

2.2.3 Alcoa Mandatory Standards (AMS)

Alcoa establishes an extensive suite of policies and procedures on Safety, Health and Environment. A subset of these are called Alcoa Mandatory Standards, guidelines which are to be implemented worldwide.

Alcoa's spray forming facilities were internally audited by a member of the Alcoa Corporate Powder Safety Committee and by experts from the Molten Metal Processing Center for compliance with the above standards. Post audit results showed areas for improvement which were promptly implemented.

3.0 DEVELOP ADVANCED DEVELOPMENT UNIT PROCESS CONDITIONS

Since the program was stopped prior to construction of the ADU, no work was performed on this task during the project.

4.0 ECONOMIC ANALYSIS

4.1 Original Proposal Analysis

Spray forming of aluminum sheet saves energy by eliminating intermediate, energy intensive, hot-rolling steps necessary with conventional ingot casting. Alcoa's preliminary analysis performed in 1992 noted that with spray forming, a savings of 4.2 x 106 Btu/ton of aluminum sheet produced could be realized over conventional processing. This could amount to a savings of 4.4 x 1012 Btu/yr of energy savings for the U.S. aluminum industry by converting 25% of the current sheet and plate production to spray forming. An even larger potential secondary energy savings (0.19 x 1015 Btu/yr.) was estimated with increased use of spray formed aluminum for lightweight automobile structures assuming 500 lbs. of aluminum usage per automobile.

The following tables were excerpted from the original Alcoa project proposal of 1992. They show a comparison of spray forming against conventional and up-and-coming processes.

Table 7 -- Potential Energy Saving by Spray Forming vs. Ingot and Continuous Casting

		Ingot Metallurgy (I/M)	Thin Strip Casting (Estimated)	Spray Forming (Projected)
Case 1 (10% Overspray)	Energy (10^6Btu/10,000 lb)	138.3	93.9	117.6 (-15%)
	Energy (10^6 Btu/lb Al)	0.0138	0.0094	0.0117
	Energy (10^6 Btu/ton Al)	27.7	19.0	23.5
	Energy (10^{12} Btu/2.1x10^9 lb)Al (projected annual production)	28.9	19.7	24.6
Energy Savings (Spray Forming versus I/M) @ \$3.50/10^6 Btu = \$15.05 x 10^6/yr				
Case 2 (0 Overspray)	Energy (10^6Btu/10,000 lb Al)	138.3	93.9	101.0 (-27%)
	Energy (10^6 Btu/lb Al)	0.0138	0.0094	0.0101
	Energy (10^6 Btu/ton Al)	27.7	19.0	20.2
	Energy (10^{12} Btu/2.1x10^9 lb)Al (projected annual production)	28.9	19.7	21.2
Energy Savings (Spray Forming versus I/M) @ \$3.50/10^6 Btu = \$26.9 x 10^6/yr				

Table 8 -- Annual Energy Savings of Aluminum Automotive Sheet

500 lb sheet Al per car,[1] 11 x 106 cars manufactured per year,[2] 1 lb weight reduction per lb of Al,1 1 gal saved per lb of Al in car lifetime,[3]
0.275 lb other Al in car per lb of total Al; 150,000 Btu/gal gasoline

	Conventional Ingot	Continuous Thin Strip Casting	Spray Forming
lb Al sheet/yr	←	$\frac{500\text{ lb} \times 11 \times 10^6\text{ cars}}{(1 - 0.275)}$ $= 7.6 \times 10^9$ lb	30% additional obsolete scrap in charge[4] over limits for conventional casting set by tramp element concentrations →
Production, Btu/yr	Base Case	0.034×10^{15} Btu	0.19×10^{15} Btu
Gasoline Savings, Btu/yr	0.83×10^{15} Btu [5]	0.83×10^{15} Btu[5]	0.83×10^{15} Btu[5]

1 Experience in Alcoa design prototypes and concepts.

2 Motor Vehicle Manufacturers Association of the United States, 1989 value.

3 On the basis that power train is correspondingly reduced in capability to just maintain vehicle performance for the lower vehicle weight; C. N. Cochran and R. H. G. McClure, "Automotive Material Design: Energy, Economics and Other Issues,"
SAE Paper No. 820149, 1982 February.

4 Whole charge weight basis.

5 This is about 1% of the 81.2×10^{15} Btu consumed in the U.S. in 1989 or about 5% of the 16.1×10^{15} Btu of crude oil used in the U.S. in 1989, Monthly Energy Review, 1990 February, Energy Information Administration, Office of Energy Markets and End Use, U.S. Department of Energy, Washington, DC 20585.

Table 9 -- Annual Conversion Cost Savings

	Conventional Ingot Casting	Continuous Casting	Spray Forming
Conversion costs ¢ /lb (Net operating cost)	29.32	27.74	26.80
Conversion costs ¢ /lb (Cash cost - Corp. charge)	33.41	30.34	29.00
Annual capacity (lbs)	1.05 B	1.05 B	1.05 B
Annual conversion costs (Cash cost- + Corp. charge)	$350 M	$319 M	$305 M

4.2 DoE Analysis

Alcoa provided input into the DoE Programs Project Benefit Spreadsheet. Two versions of this document were developed: One by M. G. Woodruff, PNL dated 1995 September 07, the second one by R. Phelps, RMCI during 1996 September. Included in the analysis were:

1. Capital investment information
2. Annual (non energy) costs
3. Energy savings
4. Waste reduction
5. Financial results
6. Market penetration forecast
7. Total energy savings
8. Total waste reduction

The above gentlemen would have reported their findings to DoE under separate cover.

4.3 Alcoa Analysis

Alcoa compiled process data from the various spray forming runs plus typical production information from casting facilities to forecast conversion costs. The analysis was started in 1998 April with the first round of data becoming available in 1998 July. The expectation would have been to add an energy efficiency analysis had the project continued.

The Alcoa analysis contains a fairly comprehensive list of inputs and outputs. Figure 30 shows a breakdown of the main items affecting conversion cost in spray forming.

5.0 PROJECT MANAGEMENT

5.1 Intellectual property

During the period of 1993 through 1998, 16 invention records were filed by the Spray Forming Team under the DoE Contract. These have been listed in Table 10. Alcoa has filed patent applications for eight of these. Note that there are instances of invention records which were combined into single applications.

Table 10 -- Spray Forming Intellectual Property Developed Under DoE Program

Patent Division Job Number (DoE Case #)	File Patent Application (Yes/No)	Title	Inventors	Reduced Practice (Yes/No)
93-0223 (S-86,854)	Yes	Non-contact Linear Nozzle for Aluminum Spray Forming	J. Righi	Yes
93-0224 (S-86,855)	Yes	Linear Nozzle for Aluminum Spray Forming	J. Righi	Yes
94-0411 (S-86,859)	Yes but dropped	Spray Deposition Process for Manufacturing Sheet	G. J. Hildeman A. Ünal F. W. Baker E. S. Miksch	No
94-0793 (S-86,857)	Yes	Slotted Linear Nozzle for Aluminum Spray Forming	J. Righi	Yes
95-0561 (S-86,858)	Yes but dropped	Strip Casting of Sheet Produced by Rheospray Deposition	G. J. Hildeman M. G. Chu F. W. Baker D. A. Granger	No
93-0223, 93-0224 and 94-0793 were combined under one patent application. 94-0411 and 94-0561 were combined under one patent application but later dropped.				
95-0336 (S-86,861)	No	Semi-diverging Spray Forming Nozzles	A. I. Kahveci	No
95-0562	Yes	Apparatus and Method of Eliminating Porosity for Spray Forming	S. J. Pien	No
95-0563	Yes	Apparatus and Method for Atomizing by Enhancing Metal Flow Control	S. J. Pien	No
95-0624 (S-86,856)	Yes	Rheocasting Slab and Strip	R. L. Kozarek	No
95-0662 (S-86,862)	No	Design for Construction of DeLeval Nozzle for Spray Forming	R. A. Slaugenhaupt	No

Patent Division Job Number (DoE Case #)	File Patent Application (Yes/No)	Title	Inventors	Reduced Practice (Yes/No)
95-0669 (S-86,860)	No	Semi-diverging Duct-Flow Spray Forming Nozzle	A. I. Kahveci	No
95-0750 (S-86-864)	Yes	Substrate System Design for Spray forming	W. Chernicoff (MIT) M. G. Chu	No
95-0924 (S-86,863)	Yes	A Linear Nozzle with Tailored Gas Plumes and Method [USSN 08/915,230]	D. D. León R. L. Kozarek A. Mansour (CMU) N. Chigier (CMU)	Yes
96-2139	No	Circular Hole - Linear Spray Forming Metal Nozzle	R. L. Kozarek, W. D. Straub, J. Fischer	Yes
97-0715	No	Nozzle Tip Shape Design for Powder Atomization and Spray Forming	S. J. Pien	No
97-1015	No	Nozzle Tip Shape for Powder Atomization and Spray Forming	S. J. Pien	No

5.2 Technology Publications

Alcoa used various technical/professional forums to promote the Alcoa/DoE Cooperative Agreement and to display the technology to those who can contribute to, or would be interested in, sheet applications of spray forming.

The following papers were presented during the period of 1993 to 1998:

1. W. H. Hunt, F. W. Baker, *Aluminum Spray Forming*, NTSC/AeroMat-93, 1993 July, Anaheim, CA.
2. F. W. Baker, G. J. Hildeman, A. Kahveci, *Aluminum Spray Forming*, iCSF-II, 1993 September, Swansea, UK.
3. M. G. Chu, *Spray Forming*, Encyclopedia of Advanced Materials, 1993 December.
4. D. D. León, *Role of Atomization in Spray Forming*, Seventh Annual Conference on Liquid Atomization & Spray Systems (ILASS-Americas), 1994 May, Bellevue, WA.
5. A. Kahveci, *Processing and Properties of Spray Formed 2XXX Aluminum Alloys*, NATO Workshop on Science and Technology of Rapid Solidification and Processing, 1994 June, West Point, NY.

6. D. D. León, R. L. Kozarek, *Use and Characterization of Linear Nozzles for Spray Forming*, Eighth Annual Conference on Liquid Atomization & Spray Systems (ILASS-Americas), 1995 May, Troy, MI.
7. S. J. Pien, R. L. Kozarek, *Modeling of Spray Forming Process for Aluminum Sheet and Plate*, Eighth Annual Conference on Liquid Atomization & Spray Systems (ILASS-Americas), 1995 May, Troy, MI.
8. A. Mansour, N. Chigier, R. L. Kozarek, *Physical Modeling of Molten Aluminum Sprays*, Eighth Annual Conference on Liquid Atomization & Spray Systems (ILASS-Americas), 1995 May, Troy, MI.
9. D. D. León, R. L. Kozarek, *Use and Characterization of Linear Nozzles for Spray Forming*, Advances in Powder Metallurgy and Particulate Materials, 1995, PM2-TEC 95, 1995 June, Seattle, WA.
10. D. D. León, *Advances in Spray Forming Technique in the Aluminum Industry*, Univ. of Puerto Rico - Mayagüez Campus, 1995 October, Mayagüez, PR.
11. R. L. Kozarek, D. D. León, *An Investigation of Linear Nozzles for Spray Forming Aluminum Sheet*, Univ. of Bremen, 1995 October, Bremen, Germany.
12. D. D. León, *Role of Atomization in Spray Forming*, Pittsburgh Section of APMI Annual All-Day Seminar & Exhibit, 1995 November, Monroeville, PA.
13. R. L. Kozarek, D. D. León, *Use and Characterization of Linear Nozzles for Spray Forming*, Euro PM'95, 1995 October, Birmingham, UK.
14. S. J. Pien, Ding, M.-K. Chyu, *Model of Droplet Flow*, Temperature and Solidification in a Spray Forming Process, International ME Congress.
15. S. J. Pien, J. Luo, F. W. Baker, M.-K. Chyu, *Numerical Simulation of a Complex Spray Forming Process*, Unpublished.
16. M. G. Chu, *Microstructure of Aluminum Alloy Sheets Produced by Spray Forming Using Linear Nozzles*, iCSF-III, 1996 September, Cardiff, Wales, UK.
17. S. J. Pien, *Modeling of Multi-Phase Transport Phenomena and Solidification in a Spray Forming Process with Linear Nozzles*, iCSF-III, 1996 September, Cardiff, Wales, UK.
18. K. M. McHugh, *Spray Forming Monolithic Aluminum Alloy and Metal Matrix Composite Strip*, Proceedings of the 8th National Thermal Spray Conference, p. 717, 1995.
19. K. M. McHugh, *Spray-Formed Tooling and Aluminum Strip*, Proceedings of the Fourth International Conference on Powder metallurgy in Aerospace, Defense and Demanding Applications, p. 345, 1995.
20. K. M. McHugh, *Advanced Manufacturing by Spray Forming: Aluminum Strip and Microelectromechanical Systems*, Proceedings of the Fifth National Technology Transfer Conference, Washington, DC, 1994 November.
21. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelsen, R. L. Kozarek, and E. J. Lavernia, *Influence of Operating Variables on Average Droplet Size During Linear Atomization*, accepted to Atomization and Sprays, 1996.
22. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelsen, R. L. Kozarek and E. J. Lavernia, *Characterization of Spray Atomization of 3003 Aluminum Alloy During Linear Spray Atomization and Deposition*, submitted to Metallurgical Transactions B, 1996.

23. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelsen, R. L. Kozarek and E. J. Lavernia, *Size Distribution of Spray Atomized Aluminum Alloy Powders Produced During Linear Atomization*, submitted to Materials Science and Technology, 1997.
24. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelsen, R. L. Kozarek and E. J. Lavernia, *Application of Phase Doppler Interferometry for Characterization of Metal Sprays Produced by a Linear Atomizer Arrangement*, ILASS-97 Meetings, Ottawa, Canada, 1997 May 18-21.
25. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelsen, R. L. Kozarek and E. J. Lavernia, *Characterization of Linear Spray Atomization and Deposition for Continuous Production of Aluminum Alloys*, 1997 TMS Annual Meeting, Orlando, Florida, 1997 February 09-13. Also accepted to Journal of Materials Synthesis and Processing, 1997.
26. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelsen, R. L. Kozarek and E. J. Lavernia, *Application of Phase Doppler Interferometry for Characterization of Sprays Produced by a Linear Atomizer Developed for Aluminum Sheet Deposition*, Proceedings of ILASS-96 (Extended Abstract), San Francisco, CA, 1996 May 19-22.
27. Y. Zhou, S. W. Lee, V. G. M^{c}Donnel, G. S. Samuelson, R. L. Kozarek and E. J. Lavernia: *Characterization of Linear Spray Atomization and Deposition for Continuous Production of Aluminum Alloys*, - Presented at the 1997 TMS Annual Meeting, Orlando, Florida, 1997 February 09-13. (Also accepted to Journal of Materials Synthesis and Processing.)
28. A. Mansour, N. Chigier, T. Shih, R. L. Kozarek, *The effects of the Hartman Cavity on the Performance of the USGA Nozzle used for Aluminum Spray Forming*, Atomization and Sprays, Volume 8, Number 1, 1998 January-February.
29. Y. Zhou, S. W. Lee, V. G. McDonell, G. S. Samuelson, R. L. Kozarek, and E. Lavernia, *Influence of Operating Variables on Average Droplet Size During Linear Atomization*, Accepted for publication in Met Trans B, 1998.
30. J. E. Fischer, R. L. Kozarek, *A Probe to Measure the Particle Enthalpy at Impact During the Spray Forming Process*, Solidification 1998, Proceedings of Solidification and Deposition of Molten Metal Droplets Session, edited by S. P. Marsh, et al., TMS Annual Conference, 1998 February.
31. R. L. Kozarek, M. G. Chu, S. J. Pien, *An Approach to Minimize Porosity in Spray Formed Deposits Through a Model-Based Design Experiment*, Solidification 1998, Proceedings of Solidification and Deposition of Molten Metal Droplets Session, edited by S. P. Marsh, et al., TMS Annual Conference, 1998 February.
32. S. J. Pien, *Modeling of Spray Forming Process*" presentation at Solidification 1998, TMS Annual Conference, San Antonio, TX, 1998 February.

5.3 Metals Initiative Holding Company

Alcoa will be the Holding Company for the purpose of holding patents and licensing technology developed under this project. As stipulated in the Metals Initiative Act, DoE transferred title of all intellectual property to the Holding Company. Attachment IV contains a copy of the Metals Initiative Holding Company Agreement. Air Products and Chemicals Inc. (APCI) was originally listed as an Industrial Participant in the Holding Company. In 1998 February Alcoa and APCI entered into negotiations regarding ownership of technologies developed under Phase I and II of the DoE Cooperative Agreement. APCI chose not to continue as a participant after reviewing their corporate strategic direction and markets. Alcoa Inc., as the Holding Company, has full title to the technology developed under Phases I and II of the DoE's Spray Forming Program.

The Holding Company will endeavor to secure patent protection for the technology developed to safeguard DoE's and Alcoa's interests. It will act as a vehicle to facilitate the transfer of technology to entities that are interested in licensing the technology, and will provide a mechanism for receiving and distributing the royalties generated from such technology.

For the purpose of receiving royalty payments and distributing such funds, the Holding Company will ensure that DoE is appropriately reimbursed for its contribution to this project. DoE will be reimbursed up to 150% of its level of contribution from the royalty revenues generated.

In support of the Holding Company, members of the Spray Forming Team will present technical papers as appropriate.

6.0 REFERENCES

[1] A. R. E. Singer, *The Principles of Spray Rolling of Metals*, Metal and Materials, Vol. 4, p. 246, 1970.

[2] A. Ünal, and D. G. C. Robertson: Int. J. of Rapid Solidification, 1986, 2, 219-229

[3] A. Ünal, *Gas Flow in Atomization Nozzles*, Physical Chemistry of Powder Metals - Production and Processing, Ed. By W. Murray Small, MS, 1989, pp. 201-228.

[4] T. Ando, C-Y Tsao, J. Wahlroos, and N. J. Grant. *Analysis and Control of Gas Atomization Rate*, Int. J. of Powder Metallurgy, Vol. 26, No. 4, 1990.

[5] N. Trentacoste and P. Sforza, *Further Experimental Results for Three-Dimensional Free Jets*, AIAA J., Vol. 5 No. 5, pp.885-891, 1967.

[6] A. A. Sfeir, *Investigation of Three-Dimensional Rectangular Turbulent Jets*, AIAA Proceedings, pp. 11-9, 1978.

[7] R. L. Kozarek, *Spray Forming Aluminum - Annual Report (Phase II) Technical Progress*, 1997 March, Alcoa Report No. C97-38411-R1.

[8] W. DuBroff, *Development of Spray Forming Process for Steel, Final Program Report*, U.S. Department of Energy, 1991 December.

[9] S. A. Moir, H. Jones, *The gas velocity profile of a free fall atomizer and its relation to solidification microstructure of collected spray droplets of 2024 aluminum alloy*, Materials Science and engineering, A173, 1993.

[10] E. O. F. Nilsson, et. al. *Method and Device for Pulverizing and/or Decomposing Solid Materials*, U. S. Patent 2,997,245 1961 August 22.

[11] Jones, Journal of Material Science, Vol. 19, pp. 1043-1076, (1984).

[12] N. J. Grant, *Casting of near Net Shape Products*, Edited by Y. Shai, J.E. Battles, R. Carbonara, and C. E Mobley, the Metallurgical Society, Warrendale, PA, pp. 203-221.

FIGURES

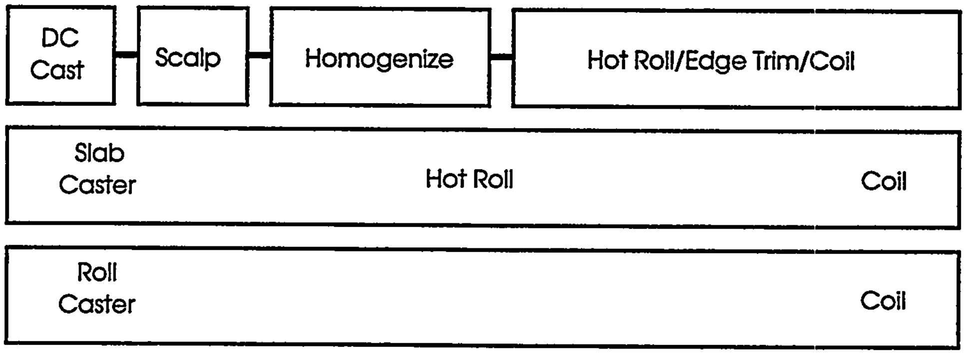


Figure 1 - Comparison of the Three Most Common Methods for Manufacturing Aluminum Reroll Stock

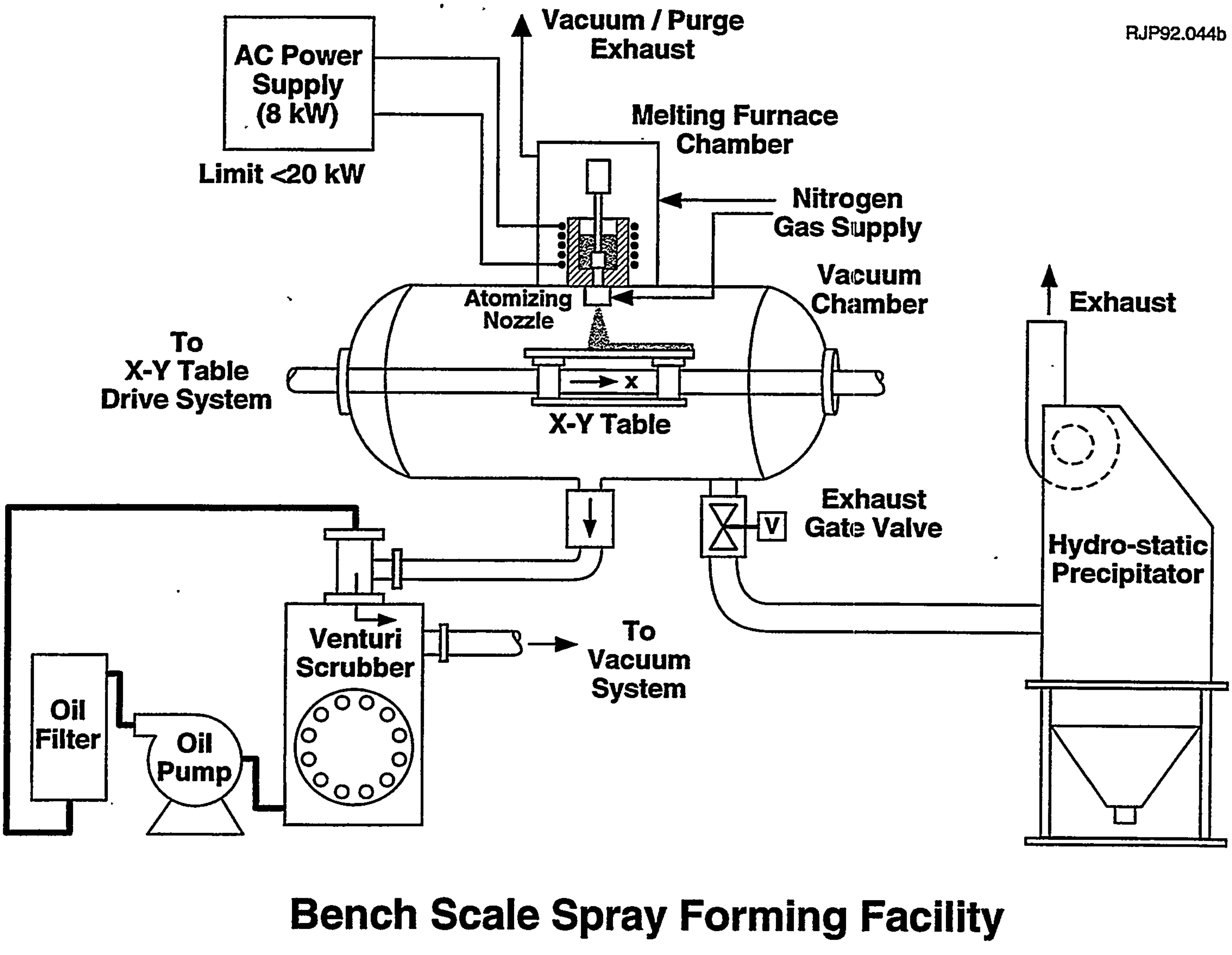


Figure 2 TAFA Vessel Schematic

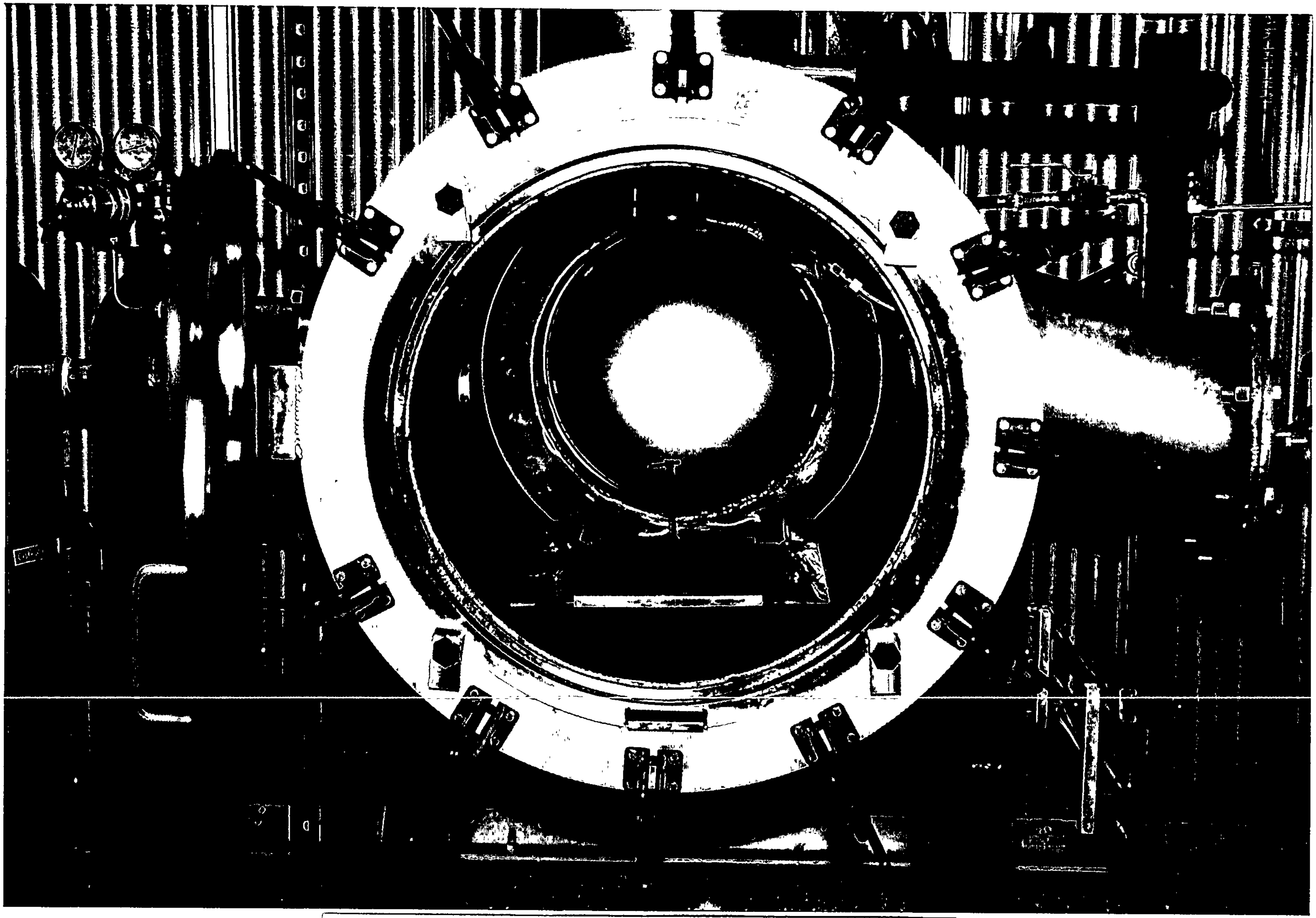


Figure 3 Photo - Inside of Marko Spray Forming Unit

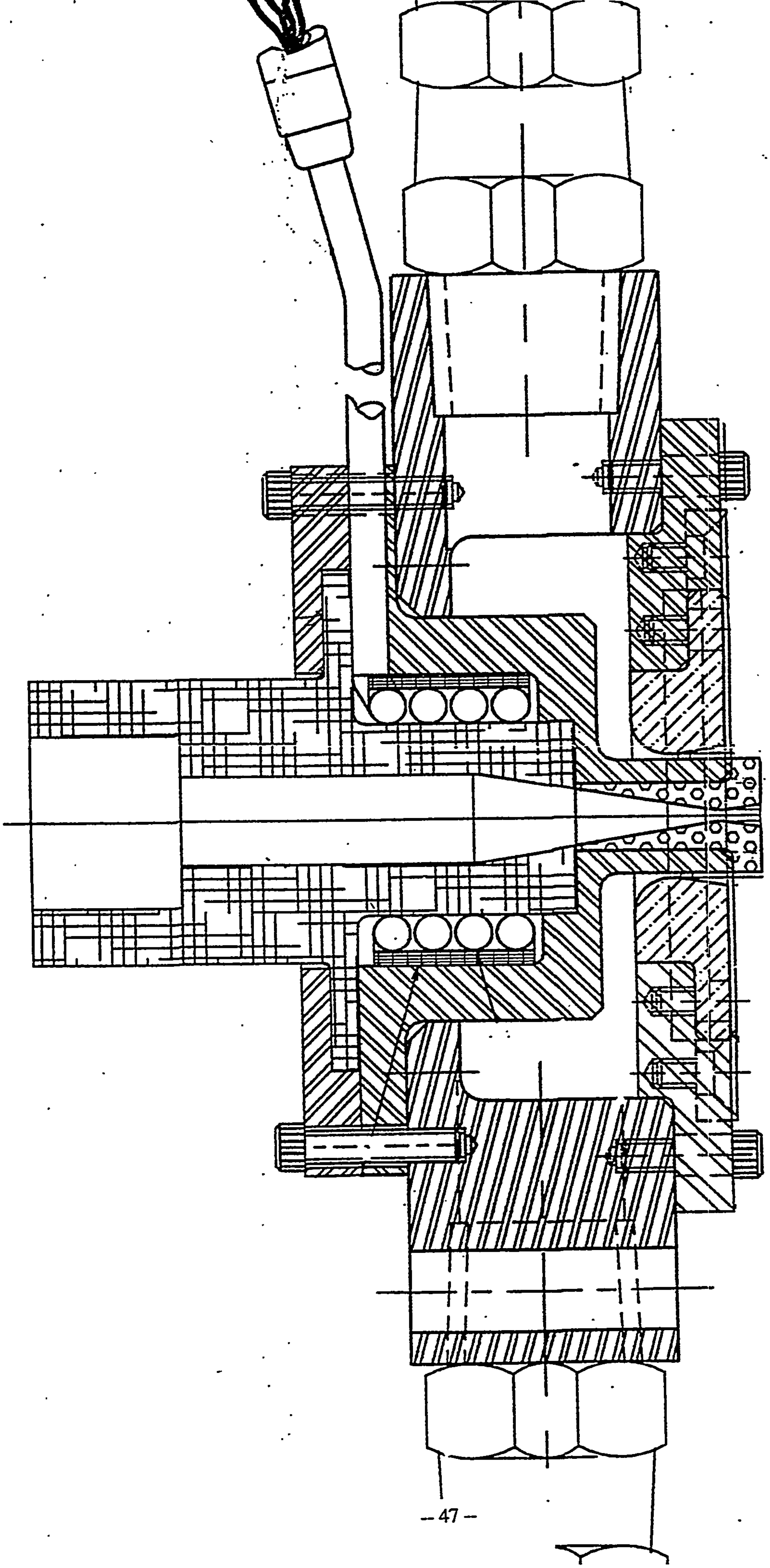


Figure 4 Schematic of Alcoa I Nozzle

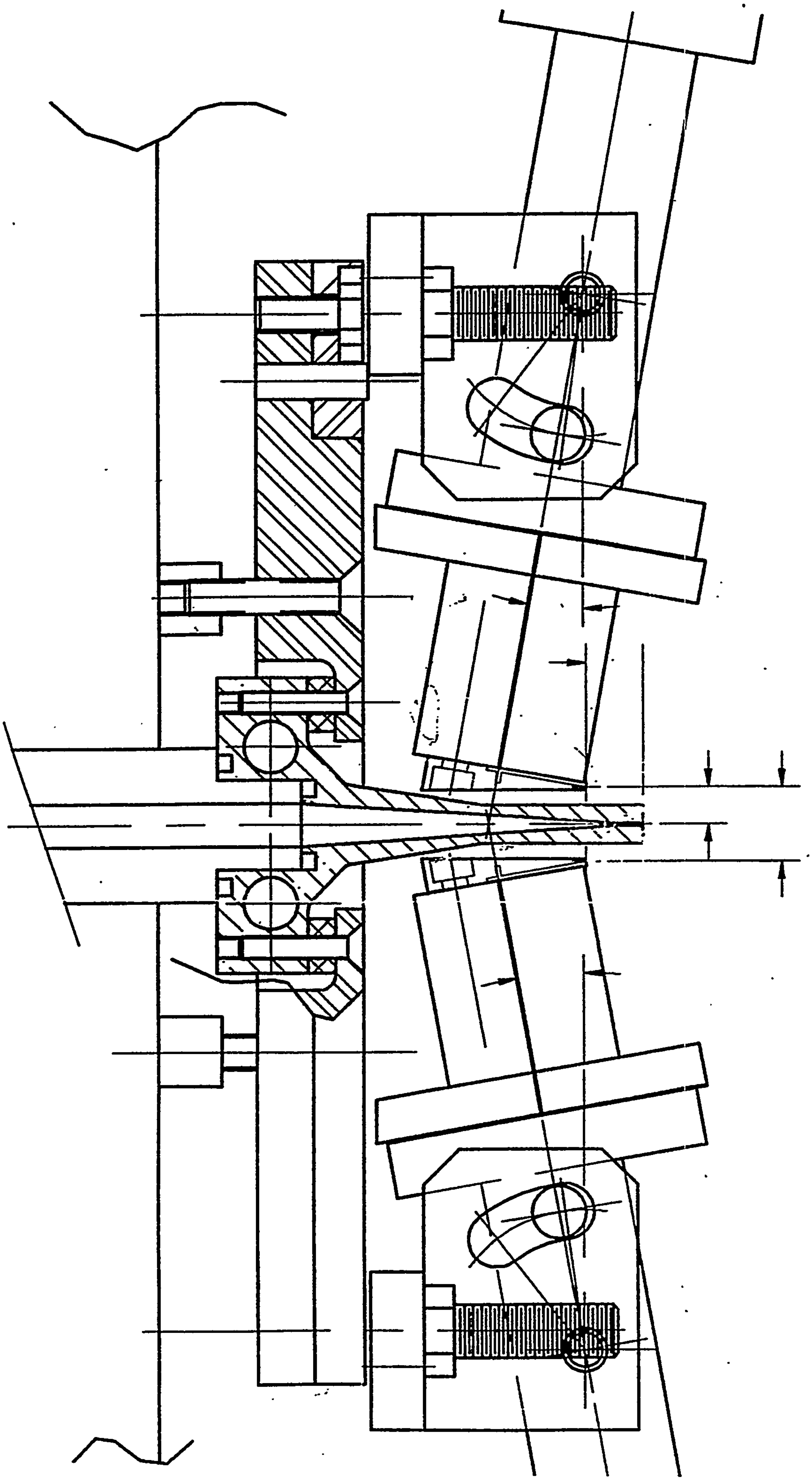


Figure 5 Drawing - USGA atomizer assembly, with mounts

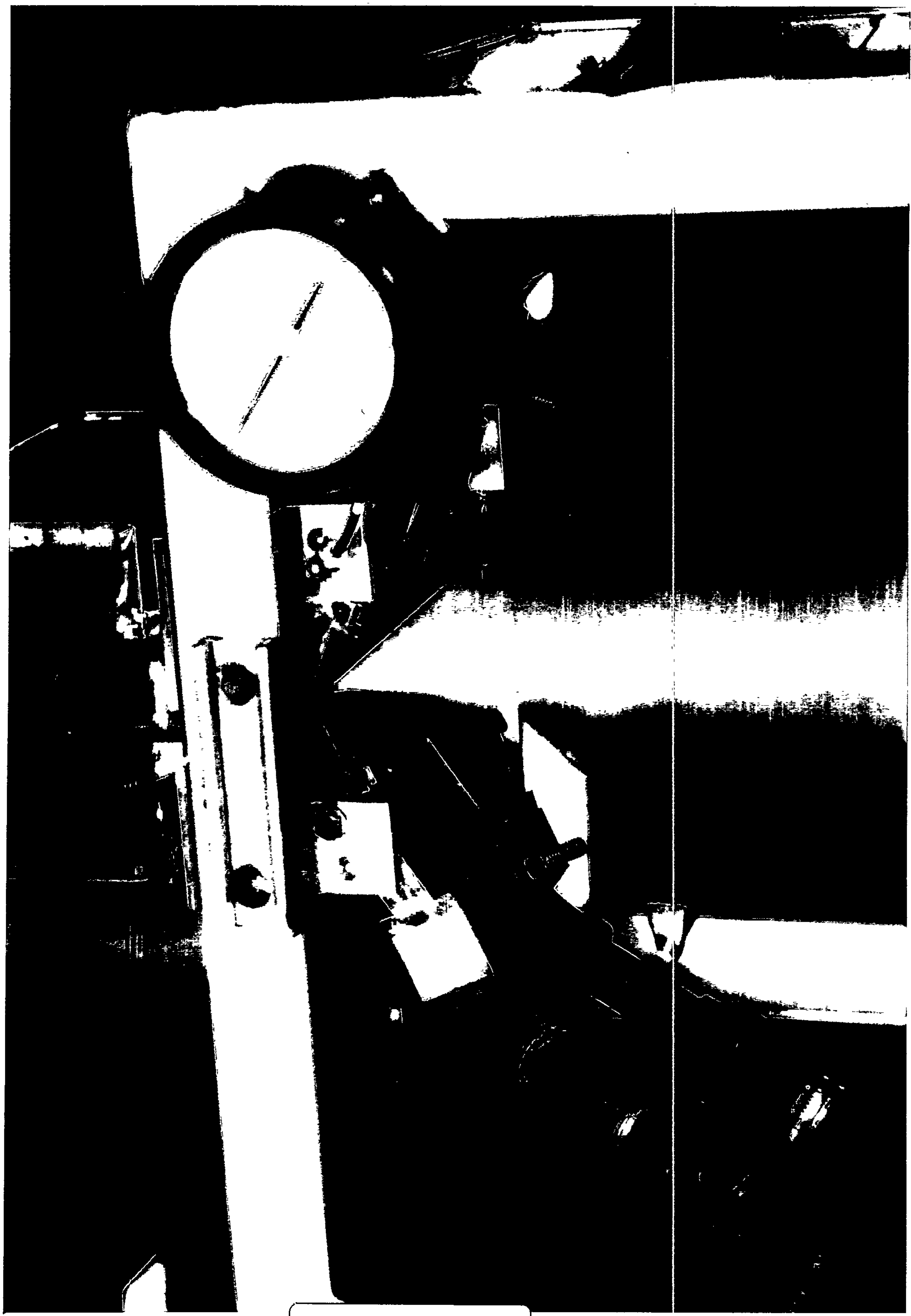


Figure 6 Photograph of 8" USGA Nozzle

Alcoa II Nozzle

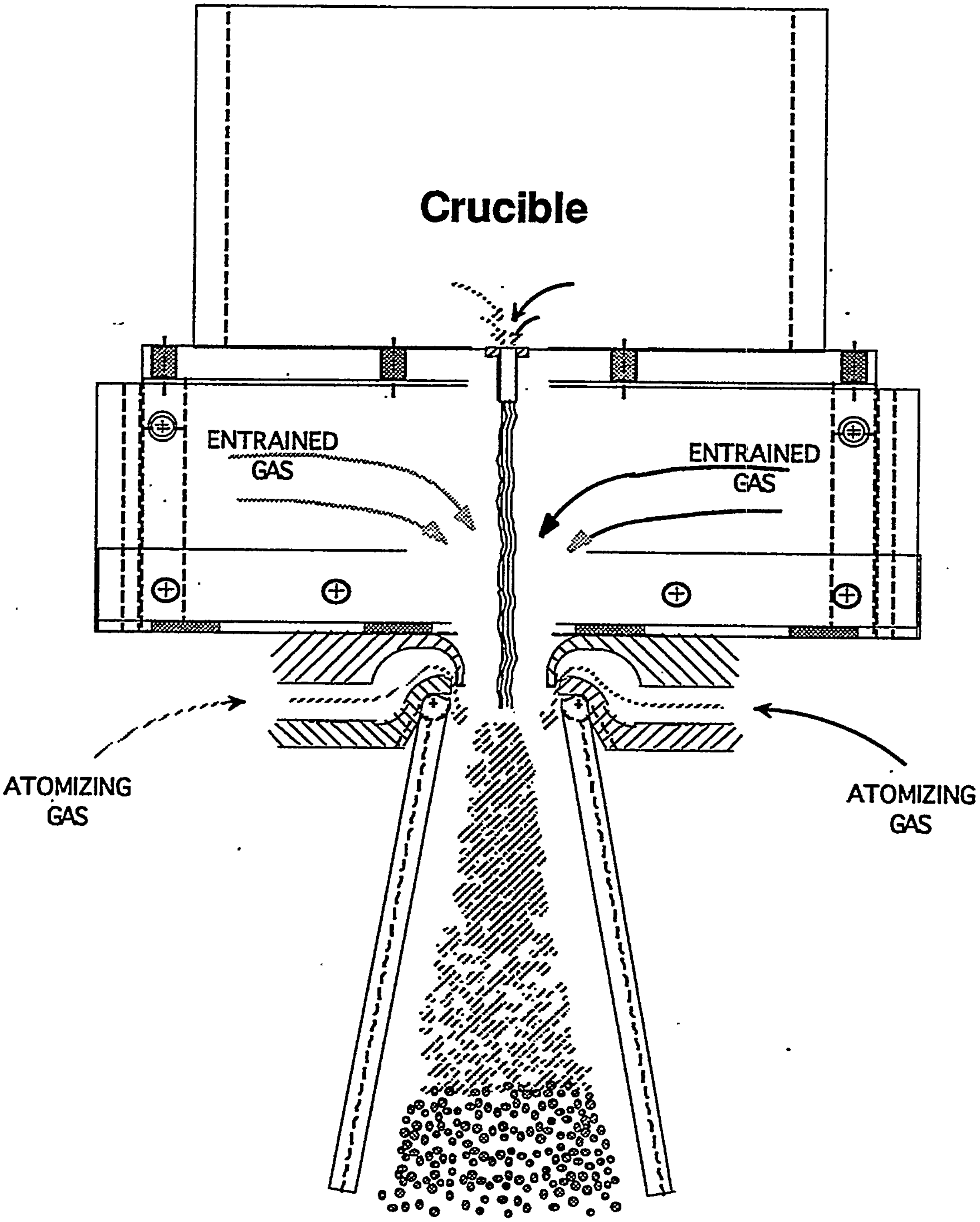


Figure 7 Schematic of 2-D Alcoa II Nozzle

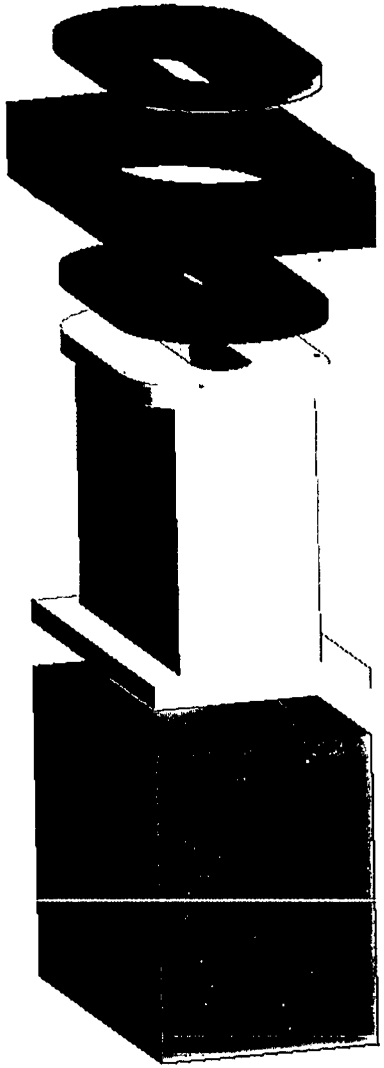
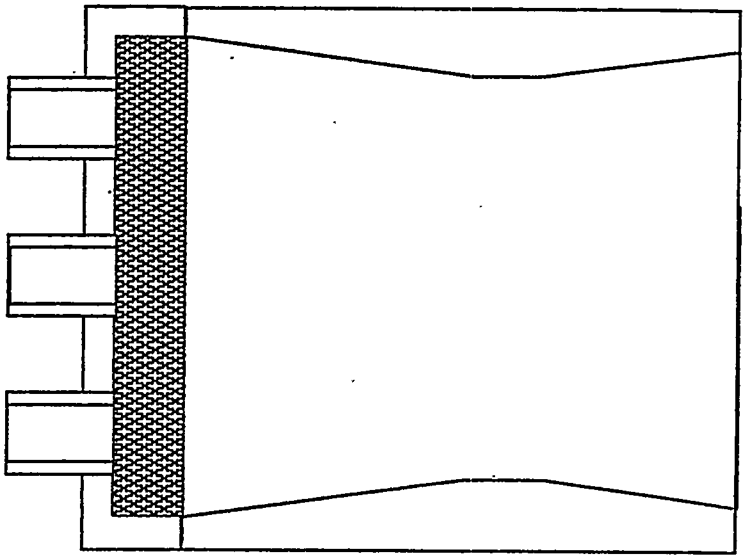


Figure 8 3-D Rendering of Alcoa II Nozzle



8"

Three headers plus screen and metal gauze

Figure 9a Schematic of 8 in. INEL Nozzle with Three Headers

8" INEL (ALCOA adaptation)

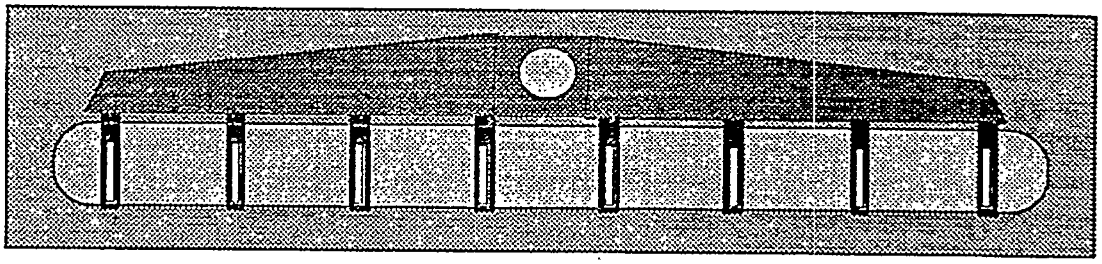


Figure 9b Metal Feed System for 8 in. INEL Nozzle

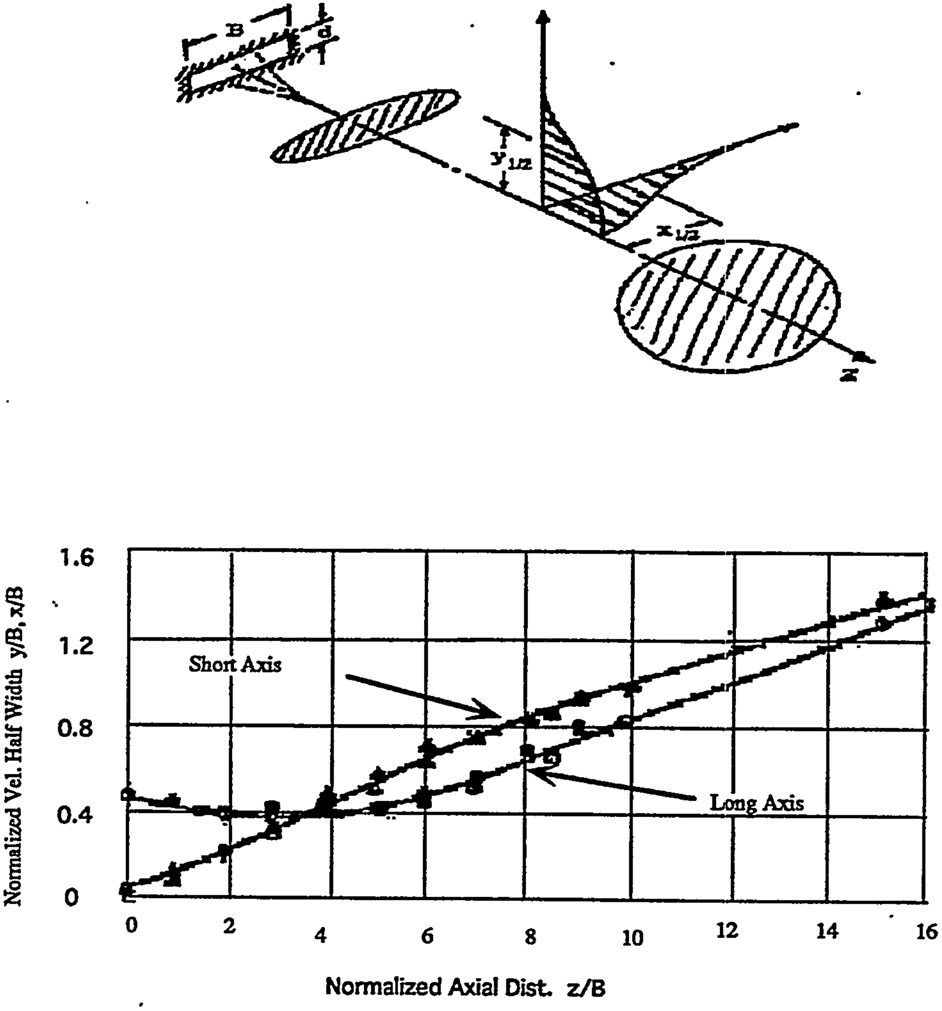


Figure 10 Axial Velocity Distribution of a 3-D Rectangular Jet

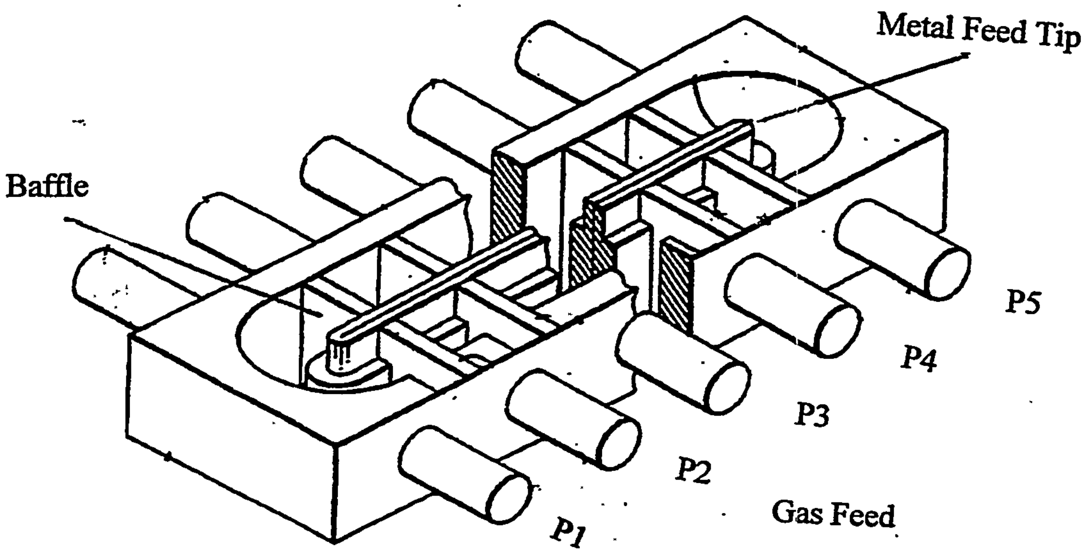


Figure 11 Cutaway schematic of Alcoa III nozzle

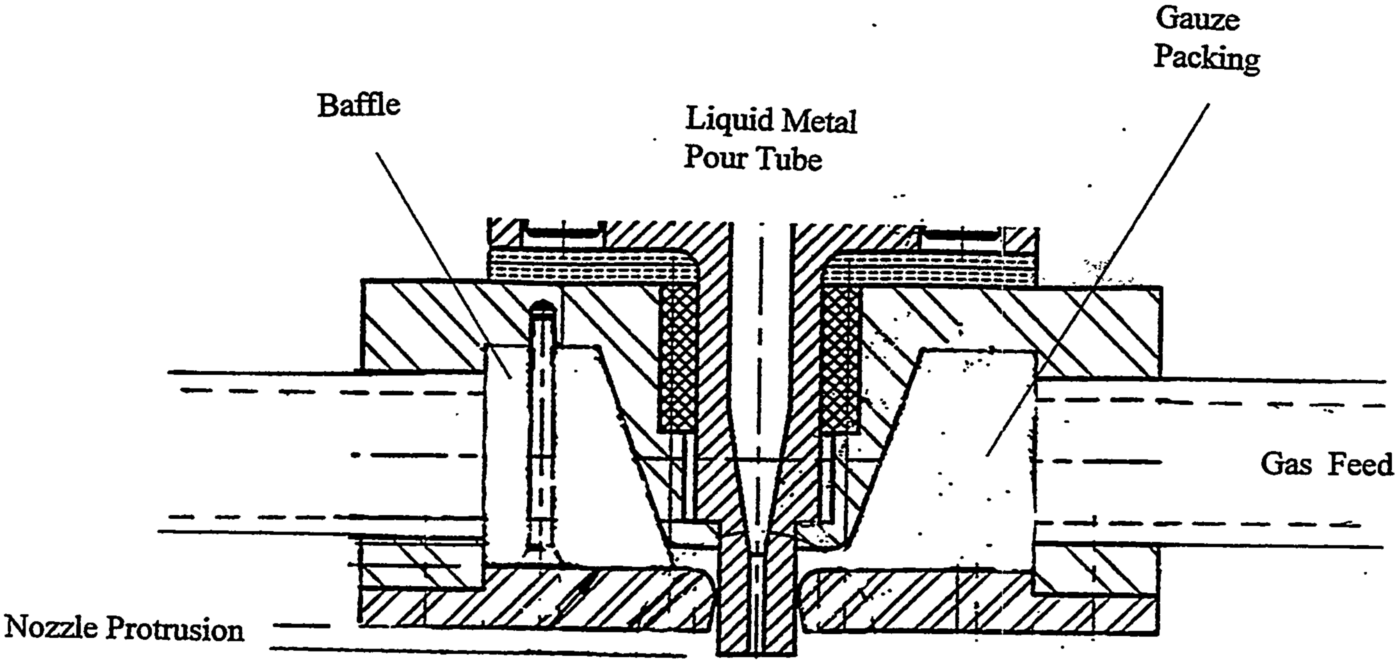
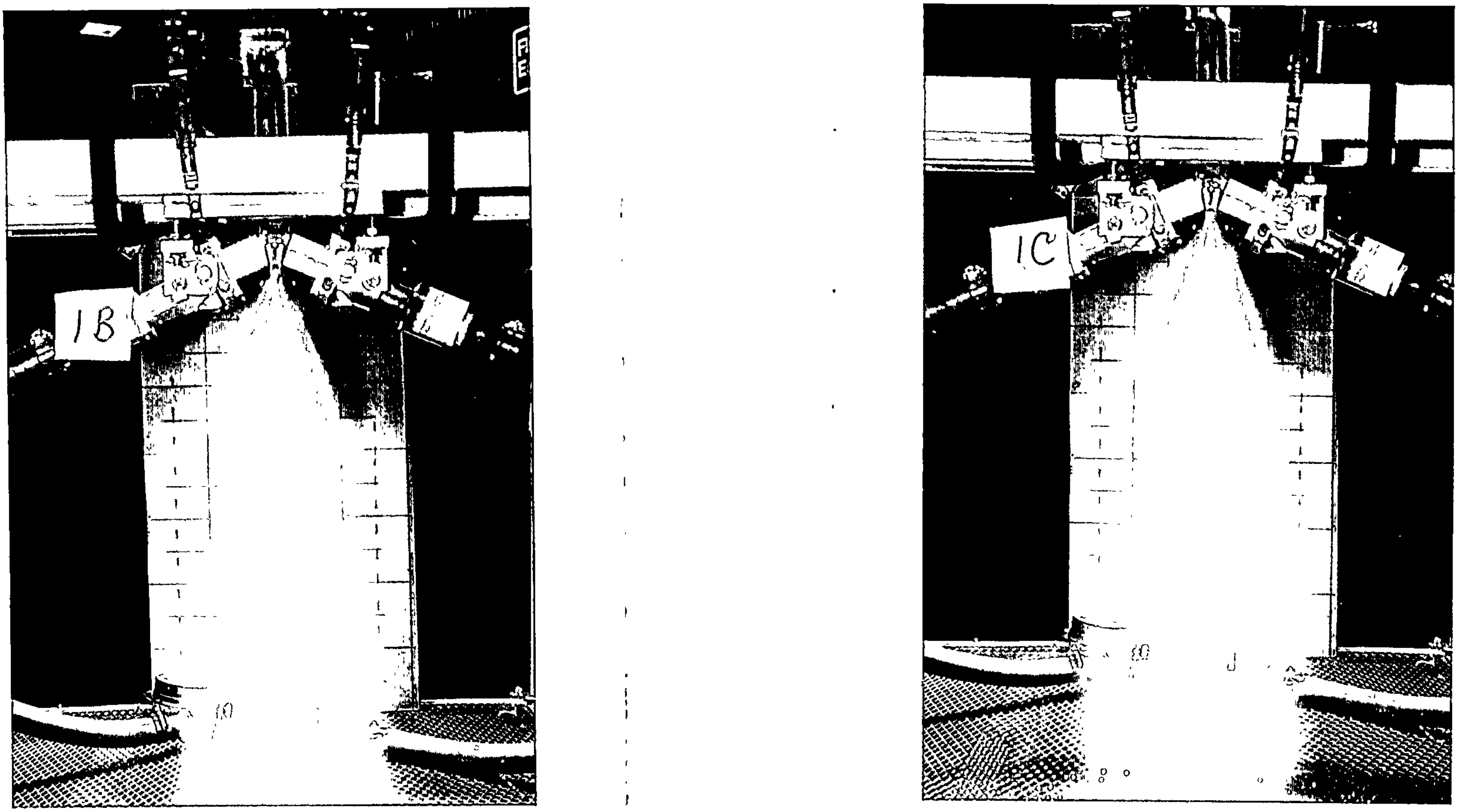


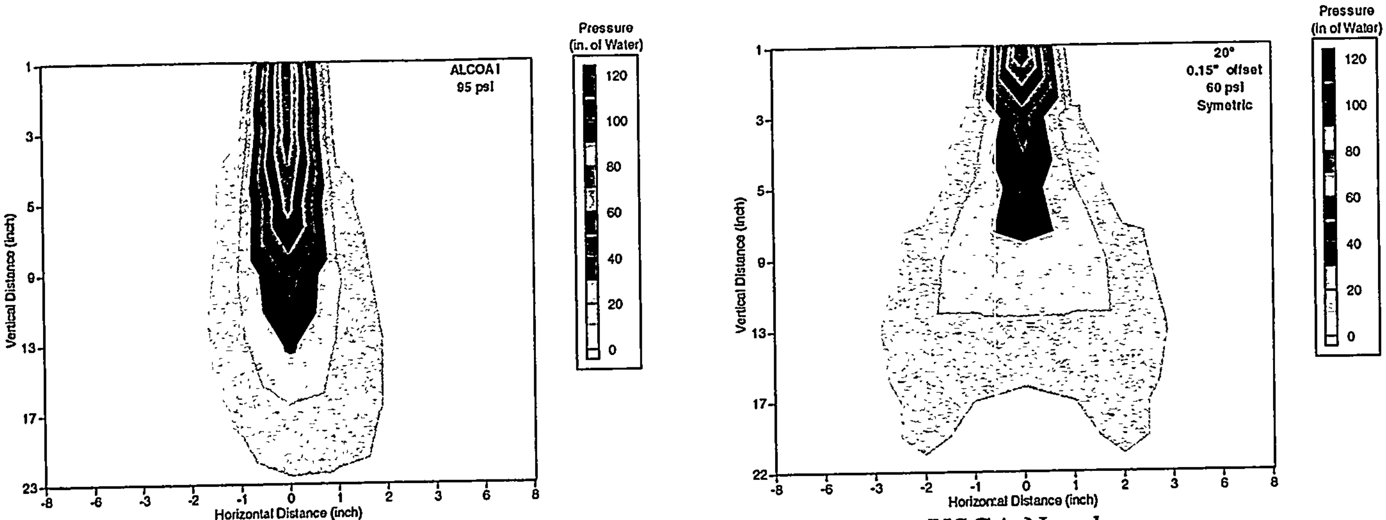
Figure 12 Transverse Section of Alcoa III Nozzle Illustrating Gas Slit Geometry



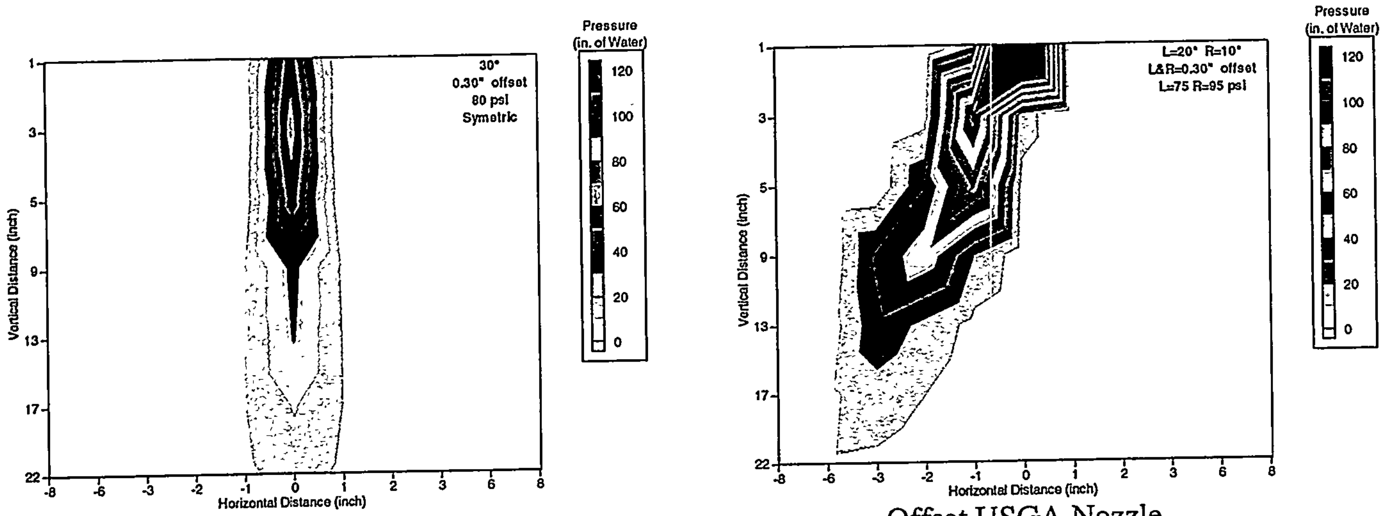
a.

b.

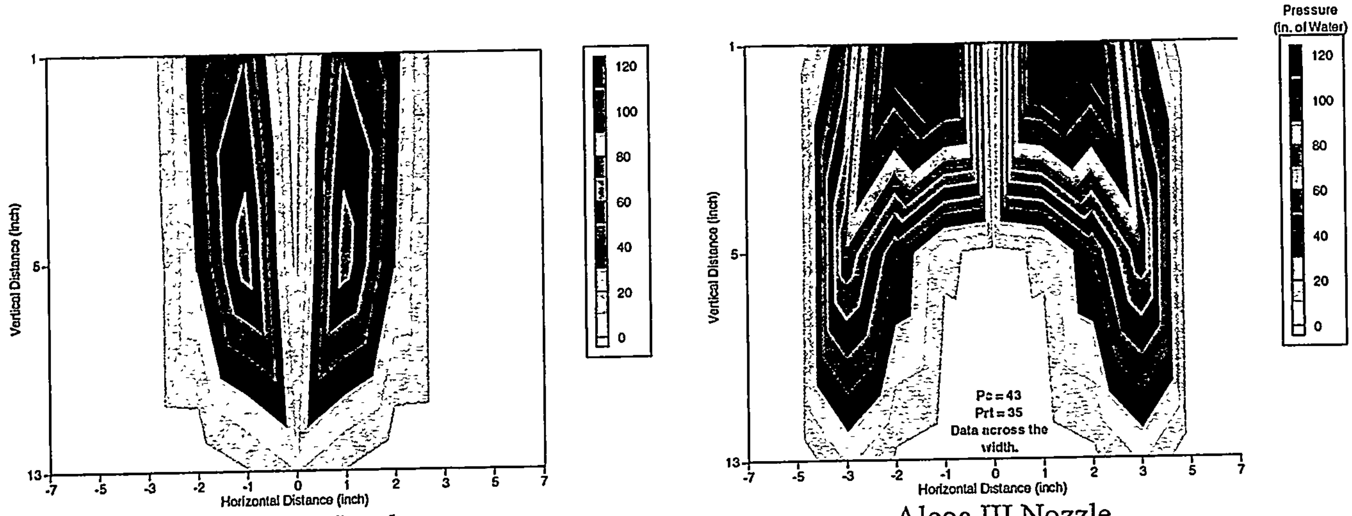
Figure 13 USGA Water Spray Photographs (a. High Gas Pressure, b. Low Pressure)



Alcoa I Nozzle USGA Nozzle

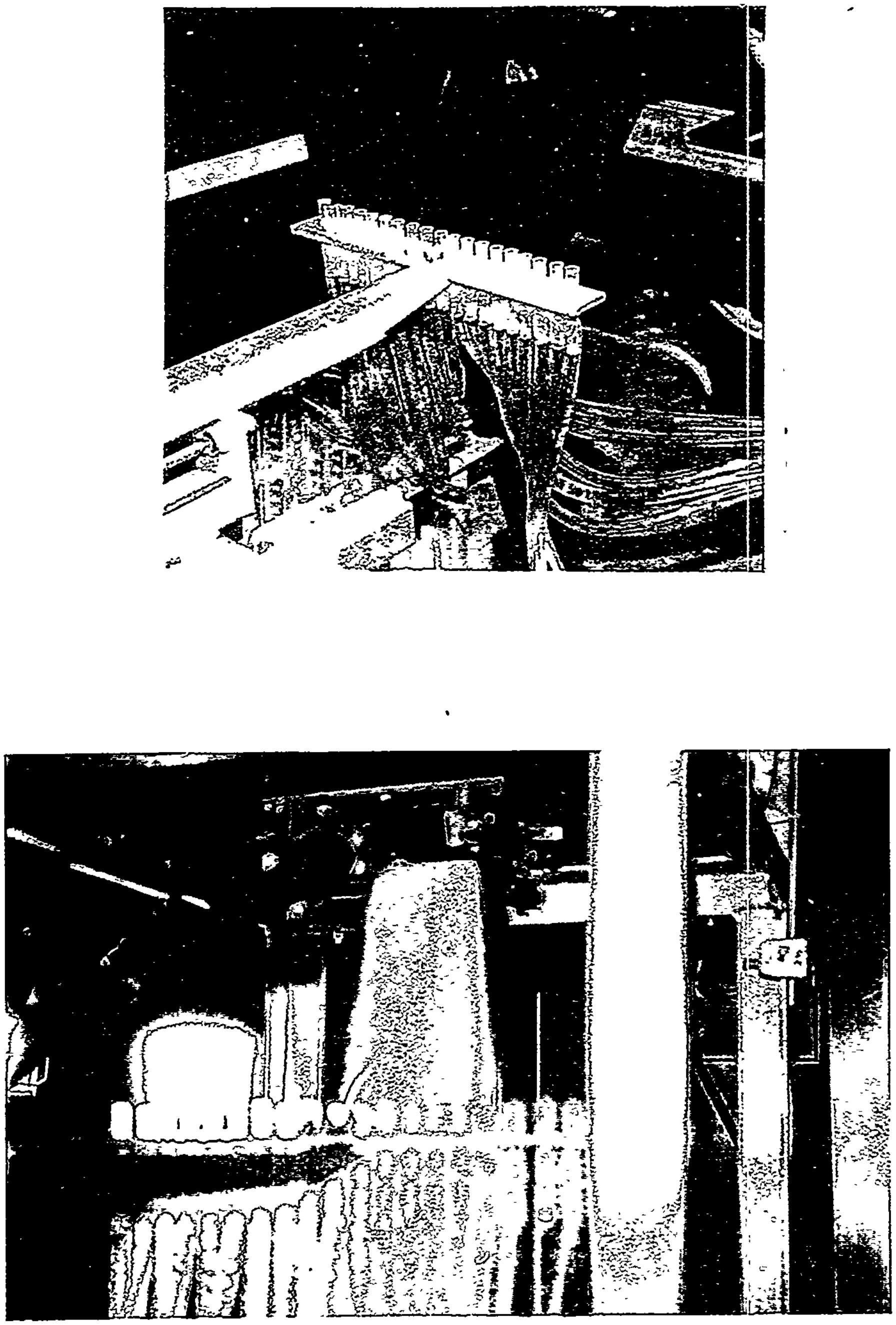


USGA Nozzle Offset USGA Nozzle



Alcoa III Nozzle Alcoa III Nozzle

Figure 14 Dynamic Pressure Profiles



Water Spray Patternator Used to Monitor the Effect of Nozzle Geometry and Process Parameters on the Deposit Profile Flatness.

Figure 15 Water Spray Patternator Apparatus

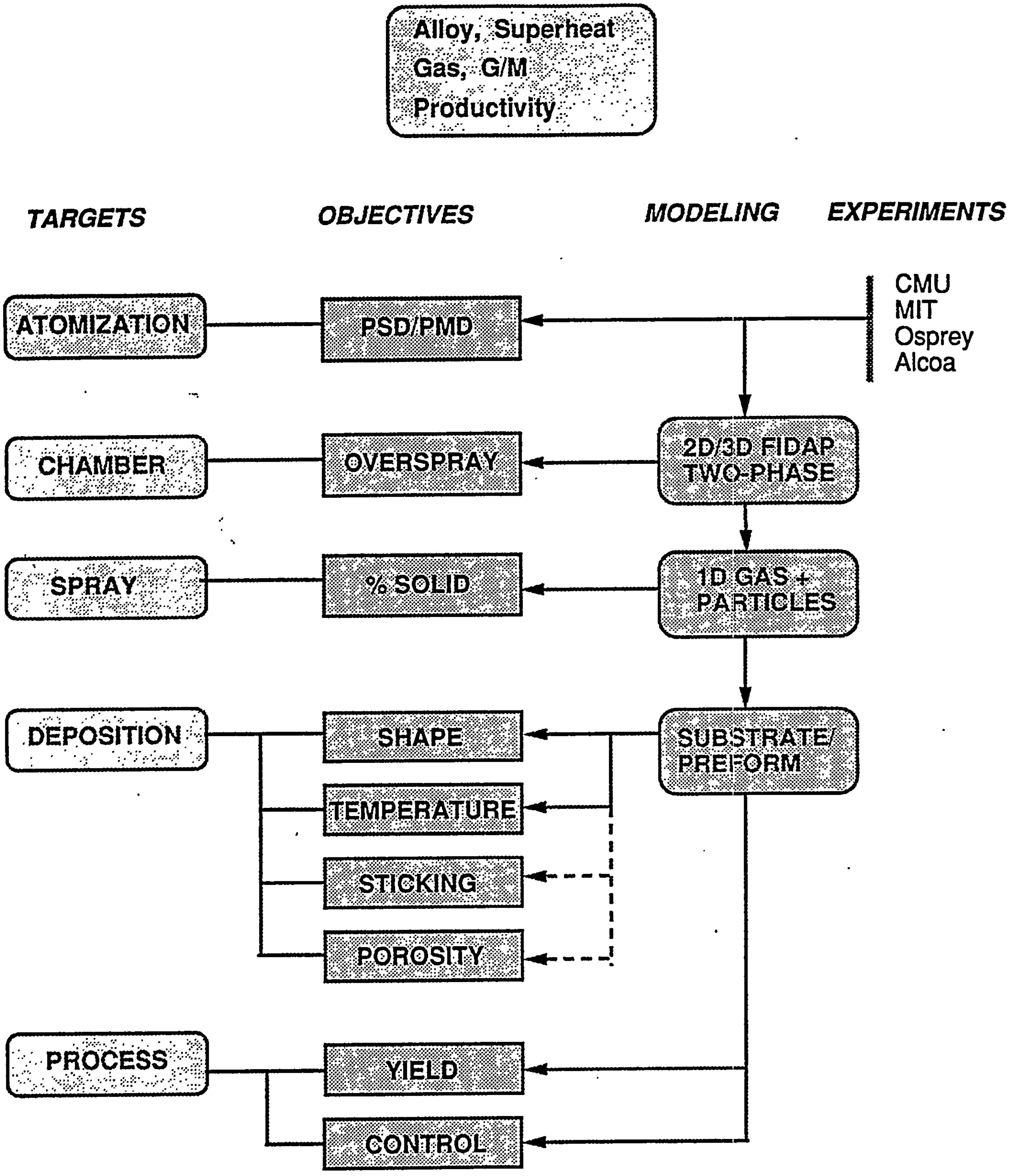


Figure 16 Framework for Spray Forming Models

Figure 17 Predicted Three Dimensional Profile of Deposit on Flat Substrate in a Large Rectangular Chamber in Surface Perimeter Form

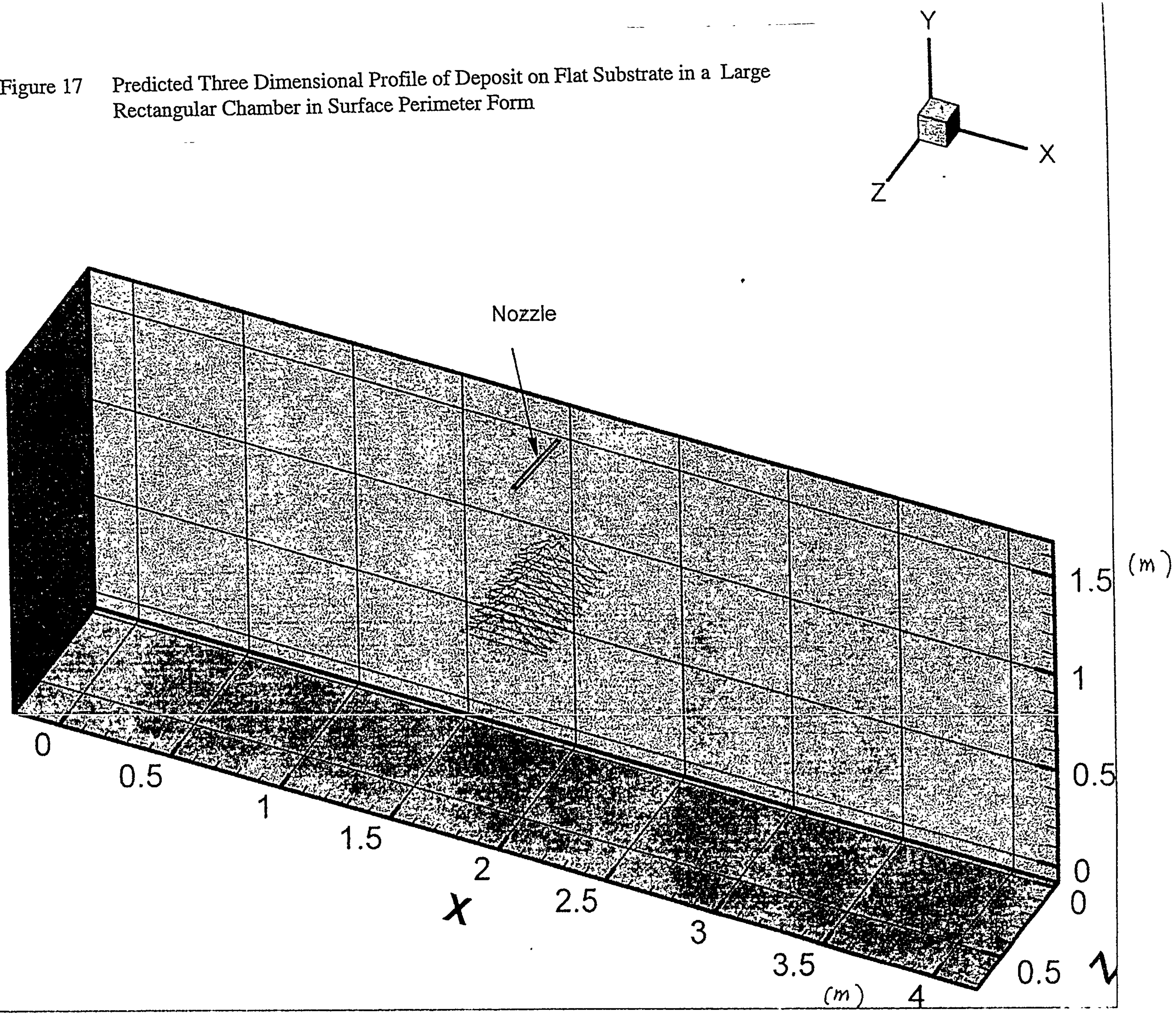
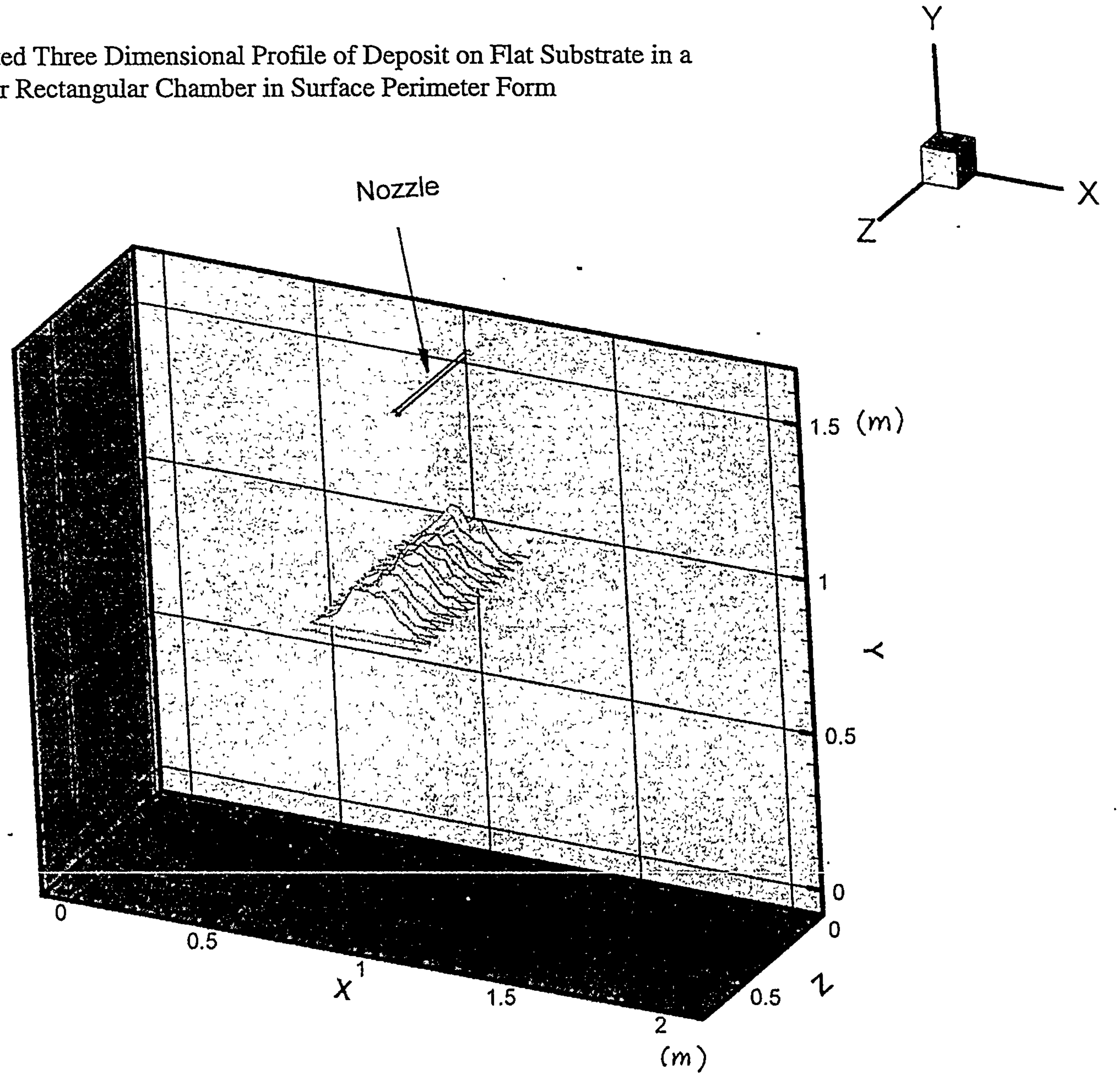


Figure 18 Predicted Three Dimensional Profile of Deposit on Flat Substrate in a Smaller Rectangular Chamber in Surface Perimeter Form



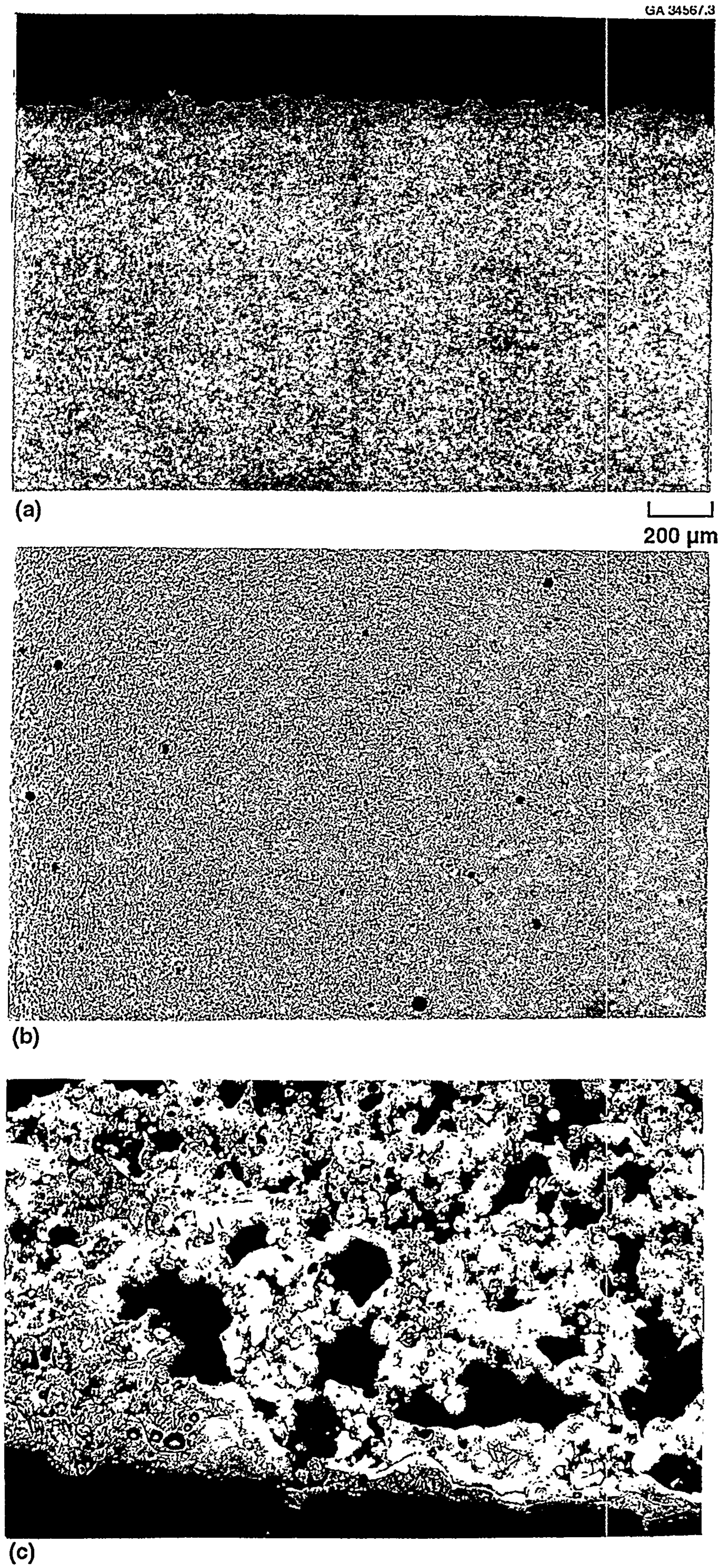


Figure 19

Typical Microstructures Observed at Three Locations through the Thickness of a 3003 Alloy at the W/2 Location. (a) The Top, (b) The Middle, (c) The Bottom of the Deposit.

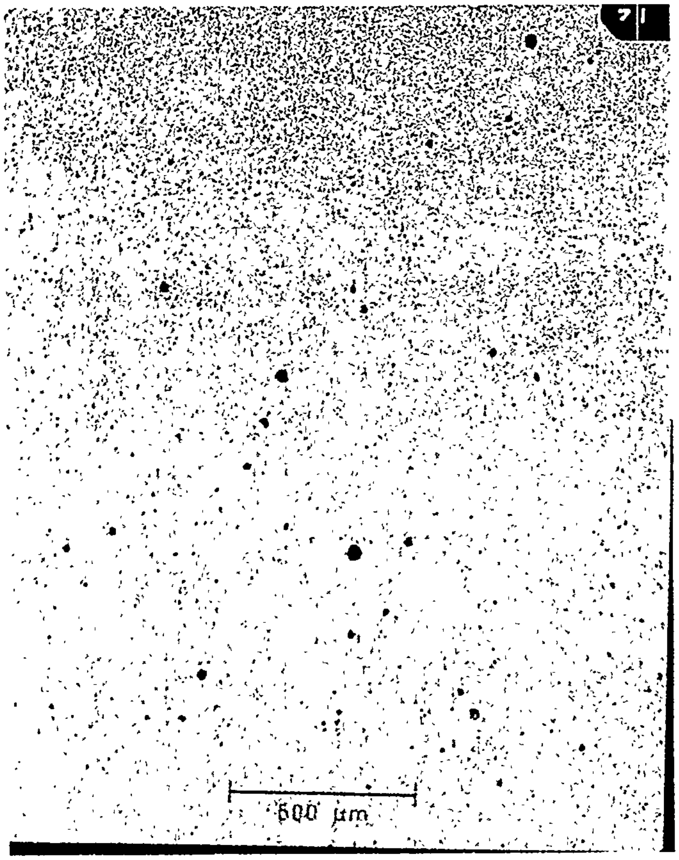


Figure 20 Photomicrograph of a 6111 Deposit - Low Porosity - "Wet" Spray - Small Pores

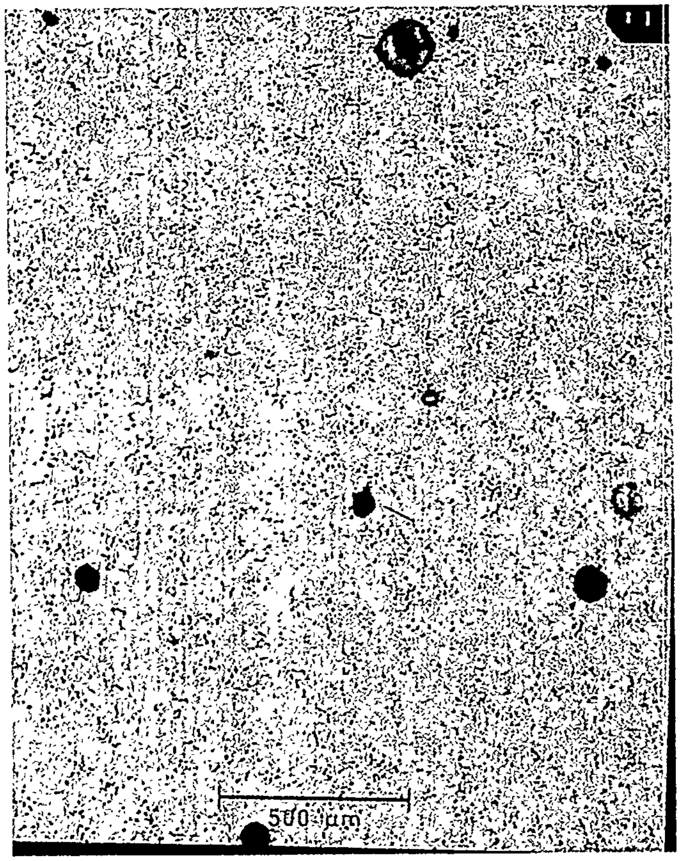


Figure 21 Photomicrograph of a 6111 Deposit - Low Porosity - "Wet" Spray - Large Pores

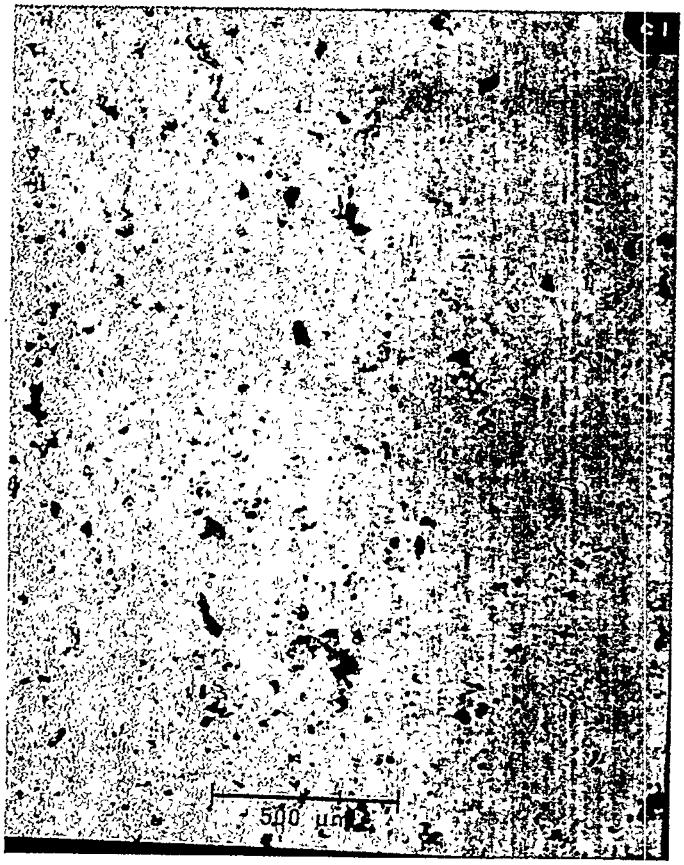
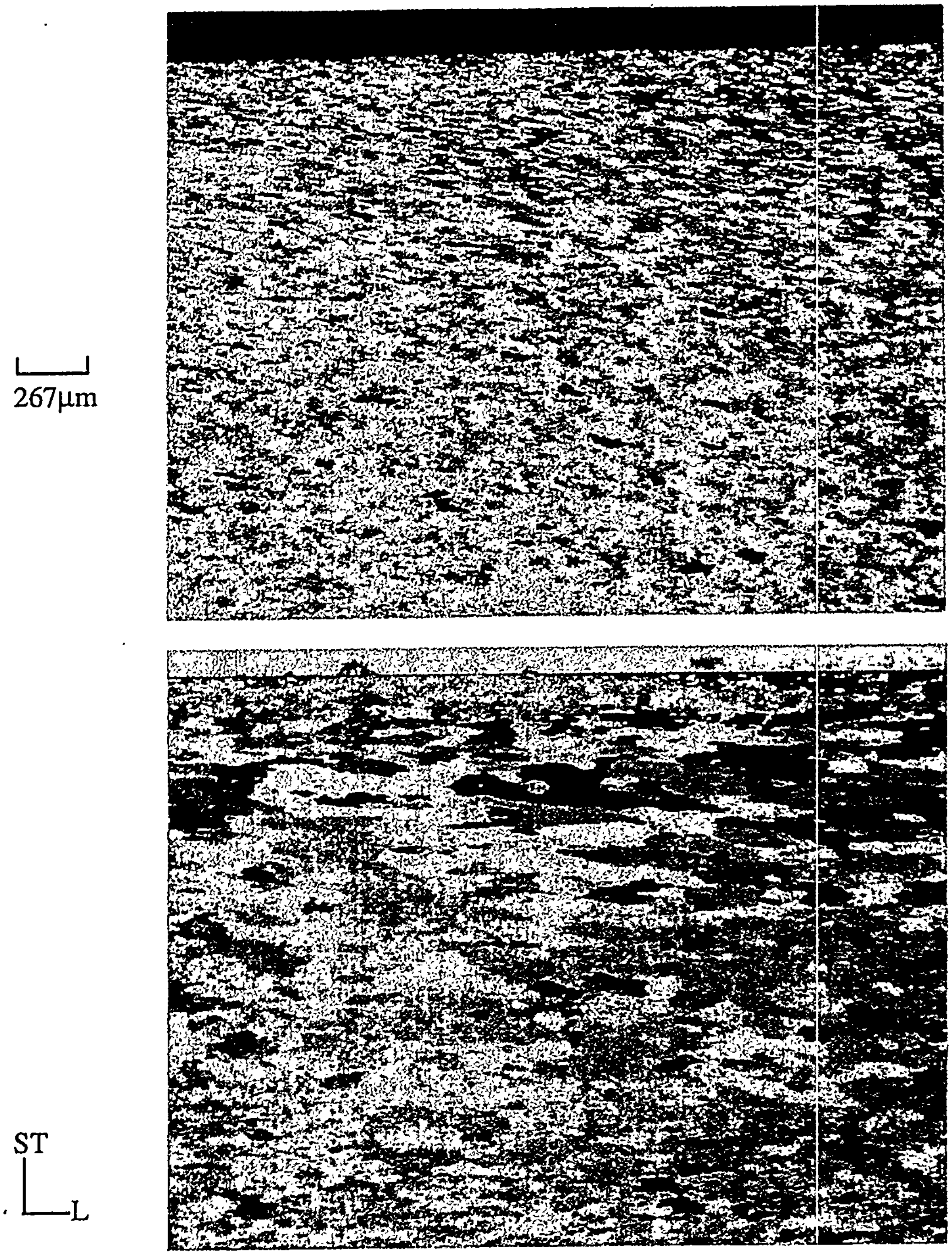


Figure 22 Photomicrograph of a 6111 Deposit - High Porosity - "Wet" Spray - Large Pores

Figure 23 Photomicrograph of a 6111 Deposit - High Porosity - "Dry" Spray

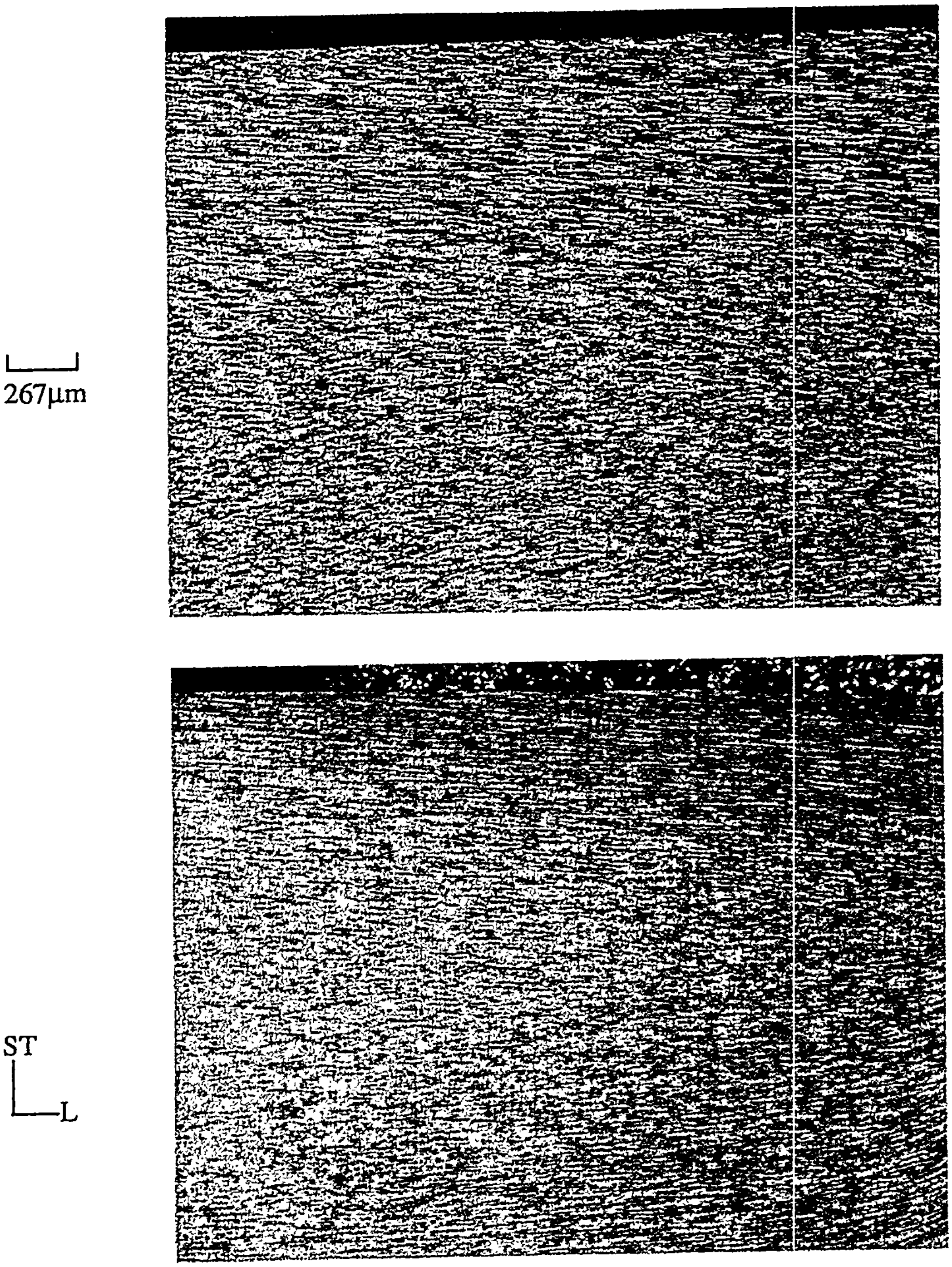


Hot Rolled
+
Simulated Coil Cool
and Gage Anneal

Hot Rolled
+
Simulated Coil Cool
and Gage Anneal

Electro etched and photographed using polarized light.

Figure 24 Effect of Hot Work Reduction and Intermediate Gage Anneal on 6111 Sheet. (Both sheets appear to be fully recrystallized as a result of the anneal.)

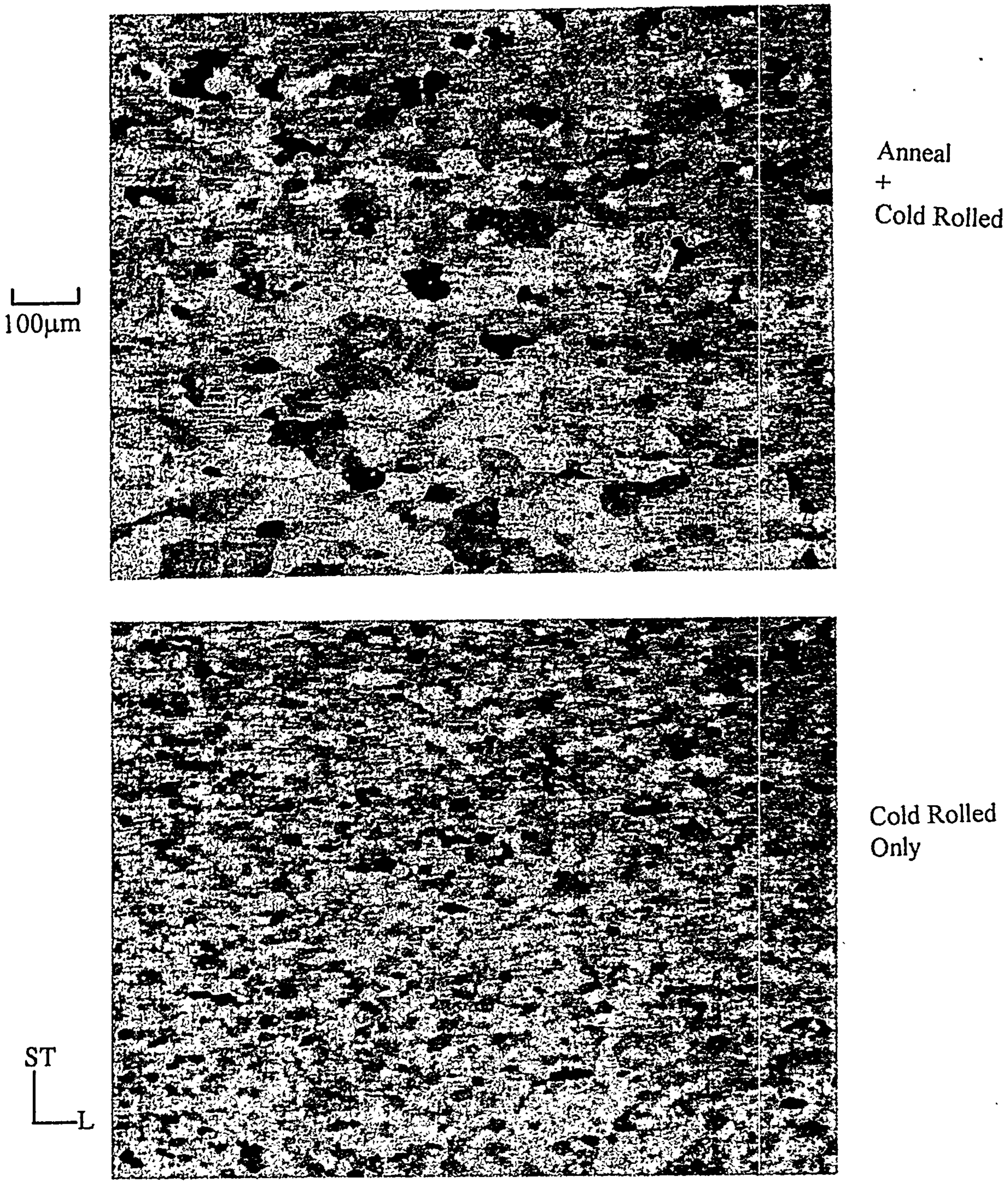


Hot Rolled
Simulated Coil Cool
No Anneal

Hot Rolled
Simulated Coil Cool
No Anneal

Electro etched and photographed using polarized light.

Figure 25 Effect of Hot work Reduction on 6111 Sheet



Etched with KM_nO_4 then photographed using polarized light

Figure 26 Grain Structure in Cold Rolled and Solution Heat Treated 6111 Sheet

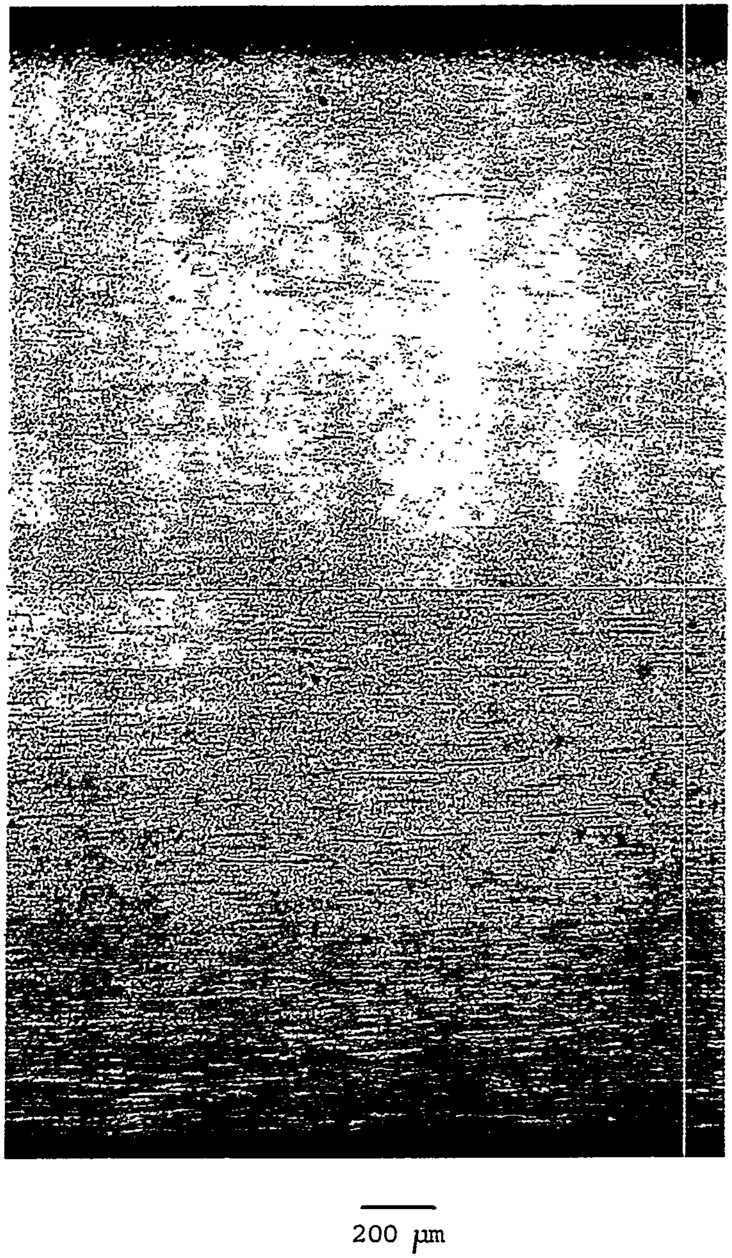
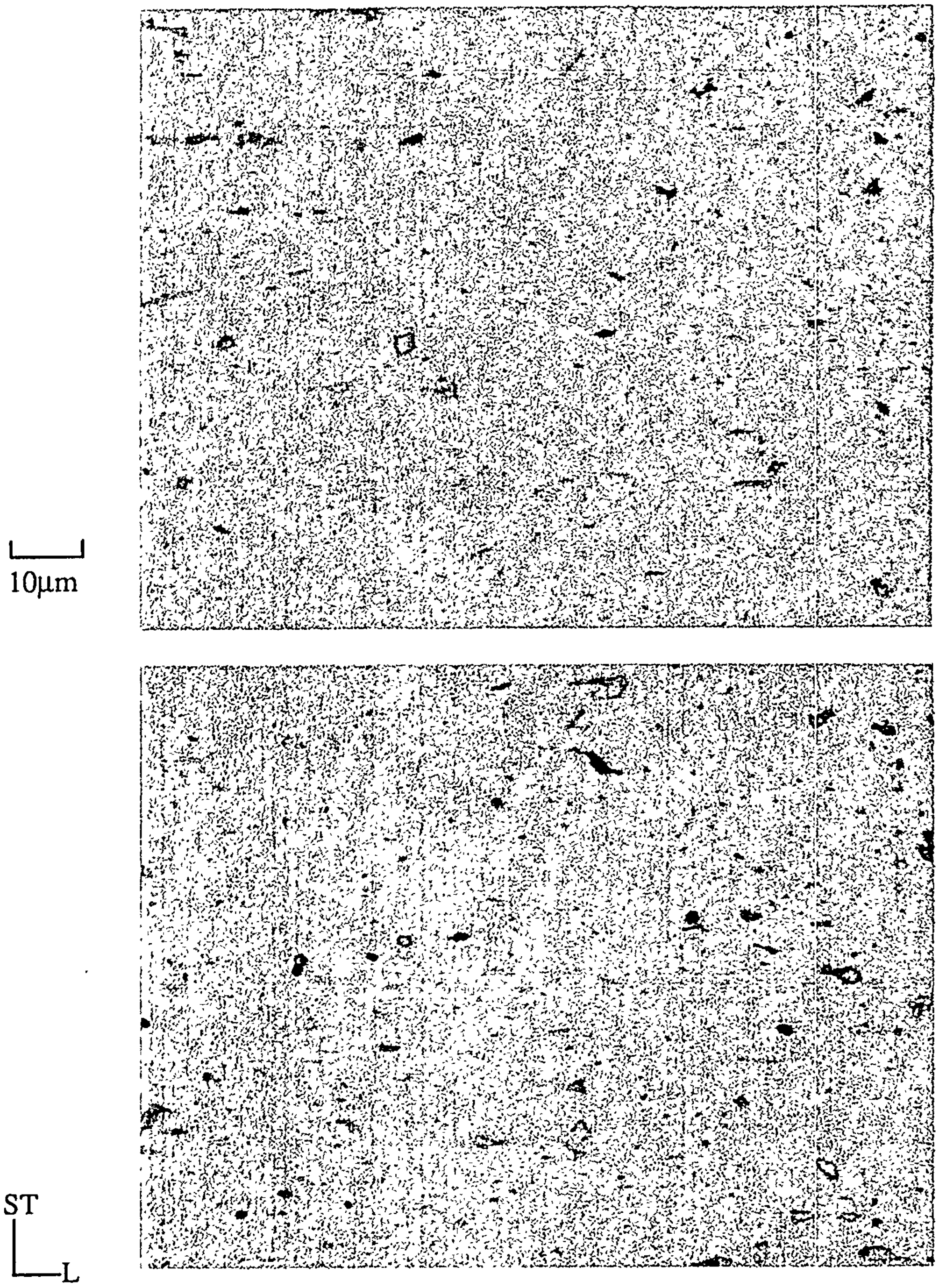


Figure 27 Overall longitudinal cross-section of hot rolled 3003 alloy after 75% reduction.



Hot Roll
Simulated Coil Cool
No Anneal

Hot Roll
Simulated Coil Cool
+ Anneal

Etched with .5% Hf

Figure 28 Effect of Intermediate Gage Anneal on Second Phase Particles. (Second phase particles appear to be coarser after the anneal. 6111 sheet after hot rolling and simulated coil cool.)

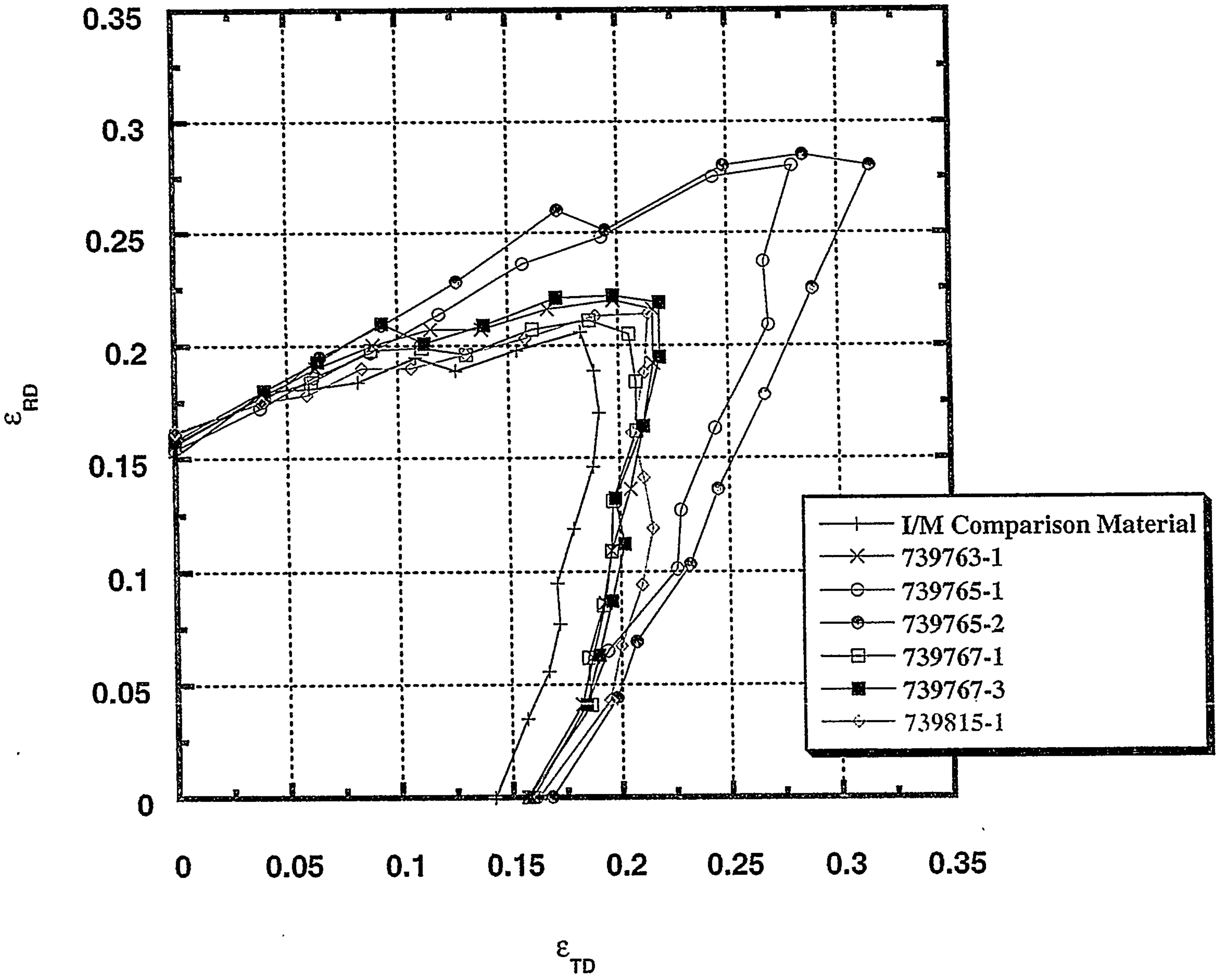


Figure 29 Texture-based FLD Prediction (6111-T4 Spray Formed Sheet)

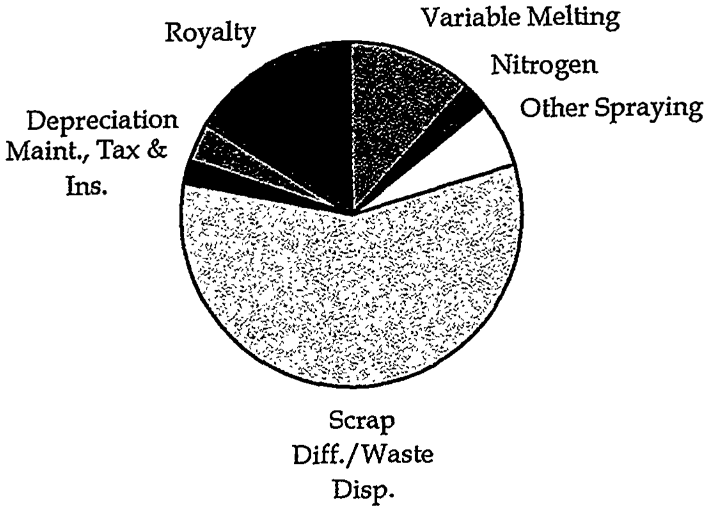


Figure 30 - Breakdown of Spray Forming of Al Sheet Costs

ATTACHMENT I

SPRAY FORMING ALUMINUM

ORIGINAL STATEMENT OF WORK (1992 SEPTEMBER)

Task 1.0 Process Development

The MIT and INEEL atomizing systems developed under Phase I will be studied along with others in this program. Representative samples of aluminum alloys 6XXX and 7XXX were produced and characterized. Further bench scale development is needed to quantify the performance of these nozzle systems before proceeding to design and construct a larger pilot plant. Initial trials will center around successful start-up and operation of the linear nozzle concept to verify the ability to generate/ control a spray plume which is suitable for strip production. Decision milestones are indicated throughout the schedule as checkpoints to evaluate and determine progress and modify future activities to meet the objectives.

Task 1.1 Process Development/Bench Apparatus

Alcoa is in the process of modifying existing equipment at Alcoa Technical Center (ATC) for bench scale spray-forming which is scheduled for completion in the third quarter of 1992. Initial experiments will employ an Alcoa-designed, 4-inch (101 mm)-wide linear nozzle followed by other nozzle systems (MIT/INEEL), as appropriate. The substrate is a water-cooled X-Y table 20x30 inch (501 x 76 cm) in size with X-axis velocity adjustable between 0.1 and 100 in/min (0.25-254 cm/min). The proposed research program on this unit includes a full parametric study of processing parameters including superheat, gas temperature and pressure, gas-to-metal ratio, spray distance, substrate surface speed and quality, roughness and cooling conditions. Initial spray deposition tests will be done with aluminum alloy 3003, and the samples will be further processed by hot and cold rolling. Mechanical properties and microstructure will be characterized, as identified in subsequent tasks, to identify optimum conditions for spray deposition and subsequent thermo-mechanical processing as a basis for pilot plant design and operation.

Alternative compositions will be investigated for alloy 3003 based on scrap recycling considerations. Impurity tolerance of the process for Fe and Si will be examined for alloys 3003 and 6061. Spray-formed material will be evaluated for mechanical properties and microstructure.

Task 1.1.1 Modify Existing Plasma Unit

Equipment Installation

A 5 kg (11 pound) capacity induction melting furnace, linear atomizing nozzle and necessary piping and controls are being installed on an existing plasma spray facility.

Conduct Initial Spray Trials

Initial spray trials will be conducted with aluminum alloy for system checkout and initial evaluation of linear nozzle performance. Major hurdles to be addressed include non-uniformity of metal leading to the linear slot, metal freezing, nozzle material performance and uniformity and profile of spray deposit. Depending on results, system adjustments and modifications will be made until feasibility of operation can be demonstrated.

Task 1.1.2 Conduct Parametric Studies

Full parametric studies will be conducted to determine the effect of such processing parameters as superheat, gas pressure, gas-to-metal ratio, spray distance, substrate material surface, speed and temperature. With appropriate diagnostic techniques and equipment, particle size distribution, particle velocities, particle uniformity across width of plume, and temperatures of droplets and sprayed deposit will be quantified and analyzed for process understanding and control.

The objective is to demonstrate process feasibility regarding nozzle design/ performance, measured parameters, and overall technical capabilities to project success in larger pilot and commercial spray forming facilities.

Task 1.1.3 Mathematical Modeling

A comprehensive mathematical model of the spray forming process will be developed to predict the droplet trajectories and thermal histories. The initial splashing of the droplets on the substrate and the joining of the new droplets into the deposit on the surface will be modeled and related to the microstructure of the deposit. The model will be used to examine how key process variables interact with each other. It will also be useful in planning experiments in the pilot plant, interpreting and generalizing the results of the tests and in optimizing the process.

Task 1.1.4 Thermo-mechanical Processing Parameters

The objective of this task is to establish thermo-mechanical processing requirements for spray-formed 3003 and other alloys as appropriate. The effects of thermo-mechanical processing parameters (roll speed, roll and material temperatures, reduction ratio, and the number of passes or stands) on microstructural evolution will be investigated. This will determine the relationship between deformation processing conditions and properties of the material in the as-sprayed and thermo-mechanically processed conditions. This program will define the range of deformation processing windows for rolling of spray-formed materials leading to products with properties meeting or exceeding the properties or characteristics produced by conventional I/M processes.

Evaluation of as-sprayed materials

The properties of the as-sprayed alloys produced in both bench and pilot plants will be characterized to determine pore size, pore size distribution, the volume fraction of the porosity and pore distribution using optical, acoustic, ultrasonic and precision density measurement techniques. The distribution of alloying elements in the as-sprayed deposit will be evaluated to define the extent of the chemical homogeneity of the as-sprayed alloys.

Development of material behavior (constitutive) model

As-sprayed materials with various initial porosity levels will be deformed in axi-symmetric, isothermal, constant true strain rate compression conditions in the cold and hot working regimes to study compaction behavior of the alloys. Reduction of porosity with strain, strain rate and deformation temperature will be quantified and the flow behavior of the alloys will be determined as a function of initial porosity level. Information gained from this study will be used to develop constitutive relations for the deformation of as spray-formed alloys of interest.

Development of rolling process model

Rolling experiments will be carried out to determine the effects of rolling parameters such as roll temperature, specimen temperature, roll speed, reduction ratio and number of passes or stands on the compaction behavior of the rolled structure. As-rolled materials will be examined to determine the extent of the compaction (the evolution of porosity) across the thickness and along the width of the rolled plate or sheet. The microstructure of the rolled materials will be further subjected to metallographic examination to determine the evolution of microstructure as a function of processing parameters. The results will be compared with the FEM predictions in order to optimize and control the rolling process. The mechanical properties of the rolled materials will be determined as a function of rolling conditions. The determination of the range of the thermomechanical processing parameters will be based on the micro-structural and mechanical properties of the rolled products.

The amount of deformation and the number of passes or roll stands required to produce fully dense sheet with desirable properties (e.g., thickness, strength and grain size), will be established prior to scaling up to pilot plant operation. This rolling process design will be interfaced with the material deformation model in order to control the thermomechanical processing of spray-formed materials during steady state operating conditions.

The rolling parameters determined in the bench scale portion of this program will be the basis of the thermomechanical processing of the as-sprayed sheet or plates under steady state spraying conditions in the pilot plant. The rolling parameters will be optimized further for the pilot plant operations, based on the equipment and material workability limits, and the product properties.

Task 1.1.5 Refractories/Material Design for Containment and Flow Control

The refractory systems required to enable spray-forming of molten aluminum are associated with four basic components: 1) the lining for the heated crucible, 2) the flow control device metering the molten metal, 3) the tundish located directly below the crucible, and 4) the refractory metal delivery slit that controls the stream of molten metal prior to atomization. The following tasks are required to select materials, design, and fabricate the refractory systems for testing and implementation:

Crucible

Materials will be selected on their ability to withstand reaction to/and wetting by molten metal as a coreless induction furnace lining. Primary linings for larger vessels are composed of dry-vibratable refractory of sufficient stability to minimize metal contamination and which offer reasonable life to ensure safe, reliable, low-cost operation. A refractory throat will be required in the bottom of the crucible for use in conjunction with a flow control device to develop a reliable seal.

Flow Control Device

Gravity-fed flow controls (i.e., stopper-rods, sliding and rotary gates, etc.) have been used successfully to control the flow of liquid steel at temperatures up to 3000°F (1647°C) without leaking. However, controlling molten aluminum with gravity-fed devices has not met industry acceptance because the relatively low viscosity of molten metal at 1400°F (759°C) causing leaking. One possible method for transferring molten metal from the crucible to the tundish is by using a steel siphon. This proposed system will require development of a siphon using refractory tubing and joints capable of maintaining vacuum-tightness during priming and continuous flow. An alternate system may be composed of a tap-hole block and trough similar to those used in transferring molten aluminum for casting.

Tundish

Various jointless, preformed crucible materials will be examined for corrosion and heat transfer properties. Graphite may be acceptable for short-term bench scale use, but may react with molten aluminum alloys (i.e., carbide formation) during longer operation in pilot scale. Another requirement will be the selection of materials and design for forming a reliable block that will seal against the metal delivery slit.

Metal Delivery Slit (Nozzle)

If coated, graphite may be suitable for short-term testing, but longer continuous operation periods may require a more stable material to resist corrosion and erosion by molten metal. It is also essential that any material candidate be non-wetted/reacted by various aluminum alloys and resistant to damage incurred by rapid heat-up and steep thermal gradients.

Candidate materials will be selected and evaluated for the above properties prior to selecting one or more leading materials for fabrication into nozzles for evaluation.

Task 1.2 Process Development - Pilot Plant

This part of the research work will concentrate on the development of safe and suitable operating procedures and optimizing the process in the larger pilot plant to be constructed under Task 2.0. The initial part of the work will be carried out on alloy 3003. This alloy, also chosen for use in the bench scale experiments, provides a good alloy system for process scale-up. Operating practices will also be developed for alloy 6061 and/or alloy 6009 in preparation for the product development program in Task 3.0.

Task 1.2.1 Experimental Program

Important process variables will be identified on the basis of literature, experience with the bench scale units and in discussions with experts in the field. An experimental program will then be prepared for a study to cover the influence of these parameters on the quality of sheet produced. Quality will be measured by such parameters as the level of porosity, uniformity of thickness across the section, and surface quality. The influence of these parameters on the level of overspray powders will be monitored. Operating windows will be identified for making sheet of low porosity on a consistent basis and with acceptable uniformity in thickness and surface quality. Sheets of promising quality will then be subjected to thermo-mechanical processing and, if necessary, the operating conditions of the pilot plant will be fine tuned to obtain optimum properties in the rolled product.

The experimental program is expected to have three stages as detailed below:

- Establish operating practice: Linear nozzles will be used and processing conditions such as metal superheat, nozzle-to-substrate distance, spacing between nozzle, gas flow rate and pressure will be set to optimum conditions.
- Overspray: The second stage of the experimental program is designed to determine the amount of overspray powder produced because of its importance in the overall economics of the process. If excessive (above 5%) by weight, we will investigate means, such as introducing additional gas jets at the end of the nozzle, to reduce overspray powder.

- Substrate: The third stage of the program will consider the influence of substrate belt material, cooling conditions, surface coatings and their effects on operation of plant and the quality of sheet produced.

Task 1.2.2 Establish Steady State Operation

The plant will be operated at steady state for a period of time in order to obtain data on such parameters as erosion behavior of the pouring nozzle from the ladle to the tundish, erosion behavior of the refractory liquid delivery system in the atomizing nozzles and belt life. The exit temperature of the sheet from the pinching rolls will be continuously monitored in these test to assess the degree of in-line heating required for full-scale commercial plant. Data generated here will also be used for cost estimates and for parametric cost projections for a commercial plant. This stage of the program will be performed on one of the two automotive alloys studied in this project.

Task 1.2.3 Develop Operating Conditions for Automotive Alloys

A short program of tests will be designed to identify optimum operating conditions for the production of automotive alloy 6009 in the pilot plant. This program will also include optimizing end product properties through thermo-mechanical sheet processing.

Task 1.2.4 Characterization and Processing of Overspray Powders

The amount of overspray powder formed and its subsequent processing are considered crucial for the economic viability of the process. Overspray will be closely monitored in the spray tests and measures will be taken to reduce or eliminate it by the introduction of additional gas jets at the two ends of the linear nozzle(s). Such jets will have to use heated nitrogen gas in order to reduce the quenching effect of the jets on the spray droplets. Several jet geometries, momenta and gas temperatures will be investigated. In addition to gas jets, electromagnetic or electrostatic technologies will be evaluated as a means of controlling droplets and minimizing overspray. Mathematical modeling will be used to extrapolate results from relatively short bench and pilot scale assemblies to determine if process yield criteria have been met.

It is considered unlikely that the overspray powders can be marketed as atomized fine powders since no market currently exists for the large variety of alloy powder compositions which are likely to be formed. Remelting of the overspray powders will be investigated. We will develop techniques to feed the powders and/or their compacts into the induction melting furnace under a suitable flux. Will also evaluate remelting yield cost and its influence on alloy composition.

Task 1.2.5 Optimize/Develop Nozzle Designs

Various nozzle designs (MIT-USGA, INEEL) will be evaluated in the pilot plant pending bench scale results with these systems. Nozzles will be fabricated and experiments conducted to evaluate the results of characterization and design studies.

Task 2.0 Design and Construction of the Pilot Plant

Task 2.1 Specify Design Criteria

A detailed specification for the pilot plant will be prepared incorporating appropriate Alcoa and industry standards for submittal to equipment builders.

Design of the Pilot Plant

The pilot plant will be designed to spray-form 500 kg (1102 lbs) of molten aluminum to be supplied from existing melting furnaces on site. Larger quantities of molten metal are available with appropriate handling equipment if longer runs or trials are needed. The sheet product dimensions are specified as 24 in. (609 mm) width and 0.1-1.0 in. (2.54–25.4 mm) thickness. At this width, the product will be representative of commercial size sheet (typically 60 in. (1.5 m) (or greater in width)) and will also be suitable for hot and cold rolling in existing rolling mills at Alcoa Technical Center. Detailed design of the plant will be developed in discussions with equipment suppliers around the systems outlined below.

Task 2.2.1 Melt delivery system

The metal delivery system will consist of a ladle discharging into a tundish with a slot-type discharge port(s) suitable for supplying metal to the linear atomizing nozzle(s). A Calidus ladle is being considered for the present pilot plant for controlled delivery of the liquid metal. Another pouring mechanism for possible consideration is the vacuum lift, heated autopour, developed recently in the UK and marketed by Pillar Industries Inc. The latter method works on the basis of a constant metal head and has potential for use in continuous operations. Control of metal flow, flow rate and feedback monitoring is required in both cases to allow for erosion of the pouring nozzle. The range of delivery rate available, the accuracy of control and the suitability of the two methods are to be evaluated before a choice can be made.

Task 2.2.2 Linear atomizing nozzles

Alcoa has designed and built a four inch wide (100 mm) linear nozzle for initial bench scale experiments. Nozzles for the pilot plant will be designed in accordance with the experience gained in the bench scale tests with this nozzle and others (MIT, INEEL). A number of nozzles operating in parallel across the width of the unit will be needed to cover a 24-inch (609 mm) wide sheet. Nozzle width and spacing between nozzles, will be determined by extrapolating from test results of a suitable bench scale model and thickness profile of a sheet produced by a single nozzle.

Task 2.2.3 Spray chamber

Fine aluminum powder forms the potential for an explosive mixture in air. Although the chamber will contain a nitrogen atmosphere while operating, there is the possibility of overspray powder coming into contact with air during stoppages and other chamber opening periods. This explosion hazard requires the chamber to be constructed of 304-type, spark resistant stainless steel. Explosion panels will relieve pressure build-up in case of an explosion. The geometry of the chamber will be so designed as to eliminate unnecessary turbulence and pockets of recirculating flow which could result in harmful hot spots in the chamber shell. The moving belt, or other substrate design, will be housed entirely inside the spray chamber. The chamber will be equipped with an exhaust line for spent gases and a close fitting exit gate for the spray-formed sheet. The sheet exit gate must not allow air ingress to the chamber during spray-forming operations.

Task 2.2.4 Moving belt

Two types of water-cooled belts are being considered. One by Hazelett and the other by Mannesmann Demag in Germany. These two designs will be thoroughly evaluated for use in the plant before selection is made. Alternatively, water cooling the rollers, rather than the whole belt, may be adequate for the present application. This could lead to a safer design. Changes to belt material, belt coatings, and to the water-cooling channels may need to be made on the basis of the results obtained in the plant during the course of investigations.

Task 2.2.5 Gas cleaning system

Spent gases from the plant will contain fine aluminum overspray powders and need to be cleaned of such particulate matter before being discharged to the environment. Pennsylvania Department of Natural Resources laws require that the concentration of particulate do not exceed 0.05 grains per dry standard cubic feet (92 mg/dry standard cubic meter) of the discharge gases. A cleaning system consisting of a cyclone and a battery of ceramic filters, or two sets of high-efficiency cyclones in series, is required to achieve this degree of cleanliness. EPA/DMR criteria, capital investment requirements and operating costs will be considered and will form the basis for selection of the appropriate cleaning system.

Task 2.2.6 Pinching rolls, roller table and coiler

The sheet will be drawn out of the chamber by means of a pair of pinching rolls and will then move through a roller table. Thicker gauge sheet will be allowed to cool on the table, whereas the thinner and longer sheet produced in the pilot plant will be coiled for subsequent fabrication.

Task 2.2.7 Gas delivery system

The pilot plant will use nitrogen gas at a typical rate of 2500 scfm during operation. A suitable gas supply system will be designed by Air Products to supply atomizing gas at the required rates and at a pressure between 70 to 150 psi(g) using liquefied nitrogen and an evaporator. No gas recycling will be considered for the pilot plant. Recycling would be an important factor for a commercial plant and would have to be considered.

Task 2.2.8 Process control system

The pilot plant will be fully instrumented to monitor and control critical process conditions such as gas flow rate, metal level, metal flow rate, molten metal temperature in the ladle, temperature of the deposit surface deposit at the point of deposition and at exit from the chamber. Surface temperatures will be measured by an infrared pyrometer. Additionally, oxygen monitors with audible alarms will be placed in the chamber to indicate oxygen leakage into the chamber. Operational parameters will be modified during spray-forming, based upon mathematical modeling and bench scale experiments.

Task 2.2.9 Overspray handling system

Overspray powder will be collected in the cyclone and filters which will be cleaned periodically. The powder will be stored safely until it is required in the remelting experiments or properly disposed. Proper powder handling methods and equipment will be included in the design specifications of the plant.

Task 2.3 Mathematical Modeling

Mathematical models which predict flow fields and heat transfer inside the spray deposition chamber will be utilized to optimize chamber design. Two and three dimensional models will predict relative strengths of the recirculating nature of gas flow and variation of mass flow rates along the axis of the atomizing jet.

Task 2.4 Safety Review

Operating procedures and safety features of the pilot plant design will be reviewed by Alcoa safety engineers and qualified consultants. Safety considerations will be included in all scale-up designs for commercial use.

Task 2.5 Construction of the Pilot Plant

Task 2.5.1 Construction schedule

A construction schedule will be agreed upon with the supplier(s) of the pilot plant. Operating permits will be obtained after the design is finalized.

Task 2.5.2 Site preparation and utilities

All facilities including utilities (power, water, compressed air) will be installed at the Alcoa Technical Center pilot plant site once requirements are known. Additions to an existing building will be required to house the pilot equipment.

Task 2.5.3 Installation and commissioning

Pilot plant installation will be performed under direct supervision of the equipment supplier to assure compliance with the supplier's specifications. Commissioning will include the testing of all important parts of the plant for certification of design criteria.

Task 2.5.4 Nozzle construction

Modifications to linear nozzle designs used in bench scale experiments will be conducted to determine how to construct new and larger nozzles for the pilot plant.

Task 3.0 Product/Alloy Development

The material development portion of the program, Task 3.0, will be conducted in three stages: 3.1 - Bench scale studies, 3.2 - Concept integration to produce commercially significant materials and 3.3 - Evaluation of materials produced by the pilot scale facility. Note that materials for Task 3.1 and 3.2 will be produced on Alcoa Laboratories' or subcontractor bench scale facilities.

Task 3.1 Bench Scale Studies

Task 3.1.1 Al-Cu Alloy Study

Deposits of Al-4.5 wt.% Cu will be spray-formed using a bench scale unit. Initial deposits will be made using parameters established in Task 1.0, and considered optimal for producing uniform, flat deposits with minimal porosity.

Spray-forming process parameters will then be varied to achieve a number of solidification structures. We anticipate the major factors influencing solidification structure to be fraction liquid at the deposit surface, which in turn is related to deposition rate and atomized droplet size. Parallel processing studies on alloy 3003 will help determine which of these factors, or others, need to be varied.

Deposits will be characterized using semi-quantitative optical microscopy. Emphasis will be placed on grain size and size of CuAl2 intermetallic phases. Processing parameters used to achieve the most rapid solidification rates will be determined from these microstructural observations.

Task 3.1.2 Al-Zr Alloy Study

Al-Zr alloys, having various Zr contents, will also be spray formed to obtain the most rapid solidification rates. At least five Zr contents will be explored: 0.12, 0.2, 0.5, 1.0 and 2.0 wt%.

Task 3.1.3 Characterization of As-Sprayed Materials

These deposits will be fully characterized including optical microscopy and transmission electron microscopy.

Task 3.1.4 Solidification and Microstructure Evaluation

Droplet solidification and microstructure evolution during spray-forming will be studied to increase process understanding. Overspray powder with a wide range of particle size will be characterized for microstructure. Experiments will be conducted to construct a fraction solid/time map. Solidification will be interpreted by intercepting droplets during flight at different distances from the atomizing nozzle for characterization. Levitation experiments with single droplets will be conducted to observe solidification characteristics and thermal history. Deposit porosity will be studied in relation to microstructure evolution.

Task 3.2 Commercial Alloy Development

Several sets of materials will be identified for this portion of the program. They will address grain refinement for improved formability in automotive sheet and increased tolerance for Fe and Si impurities.

Task 3.2.1 Select and Produce Alloy Systems for Evaluation

To investigate the effects of spray-formed grain structure on formability, automotive alloy 6009 will be spray formed and evaluated. Sheet produced by conventional ingot metallurgy methods will also be procured and evaluated as controls. Microstructural and mechanical property characterization will include optical microscopy, transmission electron microscopy, tensile testing and formability testing.

Tolerance for impurities will be studied using alloys 3003 and 6061. Combinations of Fe and Si levels will be produced for each alloy type together with an ingot metallurgy control sample.

Task 3.2.2 Characterize Alloy Specimens for Microstructure and Properties

Microstructural and mechanical property characterization will include optical micro-scopy, transmission electron microscopy, tensile testing and toughness testing. Since sheet will be produced on the bench scale unit, sheet width may be limited. Therefore, 6 in. x 16 in. (152 x 400 mm)-wide panels will be used for the toughness testing.

Task 3.3 Evaluate Materials from Pilot Plant

Once promising alloy candidates have been identified, the pilot facility will be used to produce larger quantities of sheet for evaluation. Alloy candidates to be produced include: alloy 3003 and an automotive alloy, 6009.

Production runs will be made for each material, producing sheet in three thicknesses for evaluation. Sheet widths will be greater than 16 in. (404 mm) so that standard plane stress fracture toughness measurements can be made.

The spray formed products will be characterized using the following:

- optical microscopy
- chemical testing
- tensile testing
- formability

Reproducibility, variations in properties with location in sheet, and variations in properties with direction will be studied in this portion of the program.

Task 4.0 Investment Analysis

An economic analysis of spray forming will be conducted based upon information gained from operating the pilot plant during the second half of the project. This information will be used to estimate operating costs for the full-scale commercial facility that is expected to follow this program. Information developed for the pilot plant's physical facilities and productivity capabilities will be used to estimate capital requirements for the commercial facility. Benchmarking of spray-forming versus competing processes such as conventional ingot metallurgy and current continuous casting, will be employed to determine energy and economic benefits of the spray deposition process. Market studies will be conducted with potential users and customers of spray-formed material providing additional information to justify a commercial facility.

Task 5.0 Program Management

Alcoa, as the prime contractor, will assume full responsibility for program management and execution of the project in terms of quality, costs, timeliness, safety, reporting and administrative functions. Alcoa will also assume responsibility for management of subcontract activities such as those to be performed at MIT, INEEL, and others. An experimental program plan will be developed that is consistent with the technical goals of the program, available resources, and budget. Program activity and progress will be reviewed on a quarterly basis. Technology transfer will be conducted in a variety of ways including the issue of reports, publication of papers, cooperating with DOE on news releases, patenting and licensing activities, and performing pilot plant trials for interested parties.

ATTACHMENT I (cont.)

SPRAY FORMING ALUMINUM CONTRACT NO. DE-FC07-94ID13238
REFOCUSED PROGRAM PLAN
1997 January 21

OBJECTIVES / SCOPE

The original objectives of this research were to show the technical and economic viability of an aluminum spray-forming process. Included were bench- and pilot-scale process investigations to show commercial readiness via production and evaluation of products, an economic assessment, market stimulation and expansion, and project management.

The program is currently in month 33 of the original schedule which started in 1994 April. Bench-scale studies have been focused on developing a linear deposition system that achieves stated objectives of deposit profile, porosity and yield. Flat deposit profiles have been achieved with the new eight in. wide, close-coupled, Alcoa III linear nozzle design.

Future work will focus on process scale-up and reduction of porosity in deposits. Pilot plant design and construction were delayed pending demonstration of technical feasibility in bench-scale studies. The bench-scale studies have highlighted the need for an advanced development spray forming unit which can function both as a vehicle to test concepts and as a demonstration unit which can be scaled large enough to test the commercial feasibility of the process. This unit will be the center of our scale-up activities.

The attached Statement of Work (SOW) and schedule reflects a refocusing of the original program plan based on reduced Government funding. Deposit profile, porosity, and microstructure continue to be critical issues that will be studied in the coming months. Construction of an Advanced Development Unit (ADU) is critical to achieving the experimental control and flexibility required to further this research.

The design and construction of the Advanced Development Unit is planned during 1997 with operation continuing during 1998-99.

Optional Tasks have also been identified by Alcoa's Spray Forming Team which would advance the technology and/or provided additional versatility to the program. These have been included as an attachment to the Statement of Work. These optional tasks, and the additional costs associated with them, have been laid-out by Task and Sub-tasks as described in the Work Breakdown Structure.

STATEMENT OF WORK

Major Task 1 - Improve Process Understanding & Capability

The objectives of Task 1 are to increase our understanding of the spray-forming process parameters at bench-scale. Included are nozzle optimization, mathematical modeling and performance of parametric analyzes, specification of baseline thermo-mechanical processing (TMP) parameters, and definition of the potential larger scale process operating conditions. The main focus will be on obtaining design information for construction of the Advanced Development Unit.

Task 1.1 Develop Process at Bench-Scale

Four linear nozzle configurations were evaluated and characterized during the first 15 months of this program. These included the USGA nozzle, the INEEL system and two Alcoa designs (Alcoa I and II). While all proved to be acceptable atomizing systems, none produced the desired flat deposit profile required for subsequent rolling and fabrication.

Follow-up work focused on a redesigned nozzle, Alcoa III, incorporating attributes of all systems tested, with special emphasis on control of gas mass flux to control aluminum droplet distribution across the spray plume. Sprayed deposits from this nozzle were more uniform in cross section and flatter than those produced with the other systems. The Alcoa III nozzle has been selected for scale-up and subsequent use in the advanced development unit.

Bench-scale parametric studies will be performed to define the spray-forming conditions that produce sheet of the desired properties. Given the reduced funding levels, heavy emphasis will be given to process modeling to minimize empirical testing.

> Subtask 1.1.1 Modify/Operate Existing Spray Forming Unit: The existing facility was previously modified to provide a 23 kg (50 lb) resistance melting furnace and fixtures for an 8 in. (200 mm) wide linear atomizing nozzle. An interim multi-point gas handling system was put in place to control this nozzle, but operation of the eight in. nozzle exceeds the capacity of the existing piping and gas controls. The system will be upgraded to provide control and an adequate gas supply. Spray trials will be conducted using alloy 6111. Major hurdles to be resolved include uniform delivery of metal to the linear slot, metal freezing, and spray deposit profile and microstructure.
>
> Subtask 1.1.2 Conduct Parametric Studies: Designed parametric studies will be conducted to determine the effects of nozzle geometry, gas pressure and temperature, gas-to-metal ratio, spray distance, and the speed and temperature of the substrate.

High speed photography, video imaging, particle capture techniques plus various calorimetric methods will be used to characterize the spray plume. In addition sprayed deposits will be analyzed and quantified to enhance process understanding and identify key control parameters. Tests will be conducted with both water and metal spray.

Computer models will be used in conjunction with parametric studies to reduce the number of experiments required. System adjustments and modifications will be implemented to establish the desired operating conditions.

Subtask 1.1.3 Fine-tune Current Mathematical Models: Computer models will be used to evaluate parameters which affect the initial splash of the droplets on the substrate and the joining of the new droplets to the deposit at the surface. Existing models will be used to examine key process variable interactions and develop control algorithms. The models will also be used to plan and interpret parametric studies, to plan experiments in the Advanced Development Unit, to generalize the test results, and to optimize the process.

Subtask 1.1.4 Characterize and Optimize Linear Nozzle Design: This task, in conjunction with Subtask 1.1.2, will focus on further developing the Alcoa III nozzle geometry and process operating parameters with emphasis on controlling the gas mass flux in the spray plume. In addition the use of shrouds to control entrainment will be investigated to provide the optimum system for sheet production.

Correlations will be developed to define a process map for the Alcoa III nozzle. The process map will be used to predict characteristic nozzle performance and resolve Advanced Development Unit issues. The characterization study will focus on the mechanistic aspects of the spray system design parameters on the atomization/deposition process.

Task 1.2 Specify Thermo-mechanical Processing Parameters:

A thermo-mechanical processing path will be specified for alloy 6111. As-sprayed materials will be characterized and processed. Alcoa proprietary models will be used to predict optimum thermo-mechanical processing conditions.

Subtask 1.2.1 Characterize As-sprayed 6111 Samples: The properties of the as-sprayed alloy produced in the bench-scale unit will be characterized to determine microstructural features such as grain size, constituent particle size, pore size, pore size distribution, and pore volume fraction using appropriate measurement techniques (optical, acoustic, ultrasonic, and precision density measurement). The distribution of alloying elements in the deposit will be evaluated to define the extent of the chemical homogeneity of the as-sprayed alloy.

Subtask 1.2.2 Confirm Roll Practice for 6111: Alcoa will develop a rolling practice specific to the needs of this material. Evaluation of the rolled materials using the specified practice will include optical metallography and mechanical property measurements.

Major Task 2 - Advanced Development Unit - Design and Construction

The objective of Task 2 is to design and construct an Advanced Spray Forming Development Unit (ADU). This unit will be used to bridge the technology gaps in scaling beyond the bench unit to test the commercial viability of the spray forming process to produce aluminum sheet. The unit will be designed to operate both in an experimental mode and in a semi-production mode. The ADU will be of a modular construction in which prototype modules can be easily attached to test design concepts. Modules will be developed for the melt and gas delivery system, nozzle system, spray chamber, shroud(s), overspray and cooling gas handling, and substrate system. The modules will be modifiable separately so that future plant concepts can be evaluated effectively. Advanced computer controls and data acquisition methods will be used.

Task 2.1 Design the Advanced Spray Forming Development Unit

The Advanced Development Unit will initially be designed to produce 12 in. (300 mm) wide, 0.1 to 1.0 in. (2.5 to 25 mm) thick and 60 in. (1.5 m) long sheets using a flat substrate. Melting will be done in a separate 200 lb capacity furnace to give at least two runs per melt. Modular construction will be used so the unit can be expanded in size or altered by adding additional modules as needed. For instance, if a belt type substrate is required, a new module will be designed to replace the flat plate substrate. The approach is to make the unit easily modifiable to accommodate future testing of prototypes for a commercial unit. Products will approximate commercial sheet after hot and cold rolling in existing mills at the Alcoa Technical Center. Detailed design and specifications will be developed in cooperation with equipment suppliers.

Subtask 2.1.1 Design Melt Delivery Module: The metal delivery module will consist of a separate melter/holder furnace discharging into a tundish with a slot-type discharge port(s) suitable for supplying metal to the linear atomizing nozzle. Commercially available vessels and control systems will be preferred. Feedback control of metal level and metal flow will be provided. The range of metal delivery rates and the accuracy of control system will be specified.

Subtask 2.1.2 Design Nozzle Module: The nozzle module will be based on the Alcoa III nozzle design. The module will have appropriate heaters and gas controls and provide for shrouding of the spray plume. Emphasis will be put on a robust design which can be easily replaced and maintained.

Subtask 2.1.3 Design Spray Chamber: A modular spray chamber will be designed that addresses all operational safety aspects of spray forming including air ingress, ignition sources, and geometries which minimize turbulence and pockets of recirculating gas that could result in hot spots in the chamber shell or areas which accumulate overspray powder. Explosion relief panels will be provided to minimize peak pressures should an explosion of overspray powders occur.

A modular construction will be specified in which prototype modules can be easily attached to test design concepts and to provide easy access. Modules will be developed for the melt and delivery system, nozzle system, shaped chamber inserts, shrouding and cooling gas handling, substrate system, and overspray powder handling. Inserts may be used to optimize the chamber design. Each module will be modifiable separately so that future plant concepts can be evaluated effectively. Advanced computer controls and data acquisition methods will be used.

Subtask 2.1.4 Design Substrate Module: The substrate will consist of a flat plate of appropriate width and length capable of translation speeds up to 175 ft per min. The substrate material could be changed as needed to evaluate commercial substrate materials, coatings, and cooling methods. Provisions will be made to heat and/or cool the substrate. The module will be designed to bolt to the chamber for easy replacement by a other substrate modules (for example belts). With the flat plate substrate, no provisions will be made for continuous product removal. Gas seals would have to be developed at a later time.

Subtask 2.1.5 Specify Gas Delivery System: Purchase specifications will be prepared for the gas delivery system to supply atomizing gas at the required pressures and flow rates. Use of commercially available equipment is planned, but gas recycling (necessary in commercial practice) will not be used in the Advanced Development Unit. Appropriate instrumentation and controls will be provided to interface with the process control computer

Subtask 2.1.6 Design Gas Cleaning Module: The module will be designed to ensure that spent gases from the ADU will be adequately cleaned of aluminum overspray particulates before being discharged to the atmosphere. Operation will be in compliance with all local, state, and federal environmental and health regulations. Although cyclones and conventional filters are envisioned for the commercial unit, the current gas wet-scrubbing system will be modified for operating the ADU. Environmental criteria, capital investment requirements, and operating costs will be estimated to form the basis for selection of an appropriate commercial cleaning system.

Subtask 2.1.7 Specify Process Control System: The ADU will be instrumented to monitor and control critical process parameters, such as atomizing gas and cooling gas flow rates, metal level, molten metal temperature, metal temperatures of the deposit surface at the point of deposition and along the substrate, substrate speed, gas inlet and exit temperatures, and deposit profile.

Task 2.2 Design Chamber With Physical and Mathematical Models

Two- and three-dimensional mathematical models are available that predict relative volume of the recirculating gas flows and the variation of mass flow rates along the axis of the atomizing jet. These models, in conjunction with physical models, will be used to predict the flow fields and heat transfer inside the spray deposition chamber. The results will be used to specify the design of the chamber.

Task 2.3 Prepare a Detailed Specification

A detailed specification for the Advanced Spray Forming Development Unit to be located at the Alcoa Technical Center will be prepared, incorporating appropriate Alcoa and industry standards, for submittal to equipment suppliers. The detailed specification will be forwarded to DOE for approval before commencing with construction.

Task 2.4 Safety Procedures

Safe operating procedures for, and safety features of, the Advanced Development Unit will be fully developed and approved by Alcoa safety engineers and qualified consultants. Health and safety considerations, paramount to successful operation of the aluminum spray forming process, will be included in all elements of this research.

Task 2.5 Construct the Advanced Spray Forming Development Unit

The Advanced Development Unit will be constructed and commissioned for aluminum spray forming proof-of-principle testing. Alcoa will establish a construction schedule, obtain operating permits, modify the existing building, provide support equipment and services, fabricate scaled-up spray system, and commission the facility.

Subtask 2.5.1 Construction Schedule: A construction schedule will be established and endorsed by the supplier(s) of the Advanced Development Unit. Operating permit applications will be initiated immediately after the design is finalized.

Subtask 2.5.2 Prepare Site and Utilities: All ancillary equipment, including utilities (power, water, nitrogen, compressed air), will be installed at the Alcoa Technical

Center site as soon as the requirements are identified. Necessary modifications to the existing building site to house the ADU equipment will be completed.

Subtask 2.5.3 Install and Commission: Installation will be performed under the direct supervision of Alcoa and the equipment supplier(s) to ensure compliance with vendor specifications. Commissioning will include testing of all unit operations for design criteria certification.

Major Task 3 - Process/Product Development - ADU

The objectives of Task 3 are to identify the sensitive spray-forming variables and key interactions leading to successful production of the selected alloy sheet. Included are the effect of microstructure on commercially significant 6111 aluminum alloy automotive sheet, generation of data needed to perform the economic analysis, a comparison of spray formed sheets with those produced by ingot metallurgy, and production of sheet samples for customer evaluation.

Task 3.1 Develop Advanced Development Unit Process Conditions

An experimental plan will be developed that defines the safety procedures and identifies the process parameters to be assessed during operation of the Advanced Development Unit. Nozzle configurations will be evaluated and modified as required to improve final sheet properties and to minimize overspray. The key operating parameters for automotive alloy 6111 will be identified. Process operating conditions will be modified as required.

Subtask 3.1.1 Provide an Experimental Plan: Important process operating parameters will be identified based on the literature, experience with the bench-scale spray forming systems, models, and discussions with experts in the field. An experimental plan will be prepared that defines the required safety procedures and the activities required to assess the influence of the important process parameters on porosity, uniformity of cross-sectional thickness, overspray, material properties, microstructure and surface quality. This experimental plan will be forwarded to DOE for approval before commencing operation of the Advanced Development Unit.

Subtask 3.1.2 Automotive Sheet Operating Conditions: The experimental design will be executed. Process operating conditions will be modified to improve the as-sprayed properties which affect the end-product characteristics of automotive alloy 6111 rolled sheet.

Subtask 3.1.3 Optimize Spray System Designs: Via modeling and bench scale testing, optimized geometries and operating parameters will be selected and tested on the ADU.

Task 3.2 Investigate Commercial Alloy

Commercially significant 6111 alloy will be spray formed and the as-cast material evaluated. Run data will be obtained to characterize deposit profile, porosity and yield.

Subtask 3.2.1 Produce 6111 Deposits: This automotive aluminum alloy will be spray formed in the Advanced Development Unit. Process parameter set points and control will follow those developed under Task 3.1.

Subtask 3.2.2 Characterization: Microstructure characterization of specimens produced in the Advanced Development Unit will include optical microscopy and transmission electron microscopy.

Task 3.3 Produce/Evaluate 6111 Sheet

Commercially significant 6111 alloy sheet will be produced and evaluated. The results will be compared to sheets produced using conventional ingot metallurgy.

Subtask 3.3.1 Develop TMP Parameters: The preliminary parameters developed under Task 1.2 will be used to investigate a post-deposit material processing path (i.e. thermo-mechanical process) appropriate for ADU-produced deposits. A baseline TMP practice will be developed based upon commercially available and Alcoa proprietary practices.

Subtask 3.3.2 Produce Sheet Metal: Spray formed deposits from Task 3.2 will be hot and cold rolled, and heat treated with the baseline TMP practice.

Subtask 3.3.3 Characterize Product: Microstructure characterization of ATC produced sheet will include optical microscopy and transmission electron microscopy. Mechanical properties to be measured will include tensile, guided bend and limited dome height tests.

Major Task 4 - Economic Analysis

The objectives of Task 4 are to upgrade the aluminum spray forming investment opportunities document based on data acquired during the project. Analysis of energy and cost savings and a definition of the capital cost requirements will be included to show the economic viability of aluminum spray forming and for subsequent use in developing investment and commercialization strategies.

Task 4.1 Perform Energy Savings Analysis

A mass and energy balance will be performed at the unit operation level to identify the energy savings potential of spray forming for subsequent use in the economic analysis. These energy requirements will be compared to competing processes to document the energy saving benefits of aluminum spray forming.

Task 4.2 Determine Capital Requirements

Projected capital costs for a full-scale commercial spray forming process will be compiled at the unit operation level for subsequent use in the economic analysis. These costs will be compared to capital costs of competing sheet manufacturing processes to document the relative benefits of producing aluminum sheet by spray forming.

Task 4.3 Perform Economic Analysis

The existing economic analysis will be updated, based on the data acquired during operation of the Advanced Development Unit, to assess the economic viability of a commercial-scale aluminum spray forming plant. The analysis will include a process/manufacturing flow diagram to define each step in the projected spray forming manufacturing process for aluminum alloy sheet, as well as, energy costs and credits, manpower requirements, increased product values, capital and material costs, and the return on investment. The overall economics of aluminum spray forming will be compared to conventional processes to document the advantages of this technology.

Major Task 5 - Project Management

Alcoa will be responsible to provide those management functions necessary to maintain the budget and schedule within established limits; seek early identification and resolution of technical, environmental, safety, health, and administrative issues; and maintain communications with all project participants, DOE, and its technical representatives. In addition, Alcoa is responsible to provide (directly or through subcontracts) the necessary personnel, materials, equipment, and facilities to perform and document the results of this research consistent with the Federal Assistance Reporting Checklist and the Experimental Plan. Finally, Alcoa will provide DOE early warning of any perceived needs to revise any of the terms and conditions of this agreement. Technology transfer will be completed through formation of the Holding Company, reporting, publishing papers, preparing and issuing news releases, patenting and licensing, and performing trials for interested parties.

SPRAY FORMING ALUMINUM
CONTRACT NO. DE-FC07-94ID13238
OPTIONAL TASKS

SCOPE

The Technical and Cost Proposal presented here reflects a severely reduced scope due to current budgetary constraints. After a review of the Spray Forming of Aluminum Cost-To-Complete Proposal submitted in 1996 October, the Alcoa Team has identified a series of Optional Tasks which would further expand our knowledge base.

The objectives of the Optional Tasks fall into three (3) general categories:
1. Increased capabilities to further our process development knowledge
2. Increased versatility of the Advanced Spray Forming Development Unit
3. Additional inventories of 6111 sheet material and/or parts with more complex property characterization.

The enclosed **Statement of Work - Optional Tasks** follows the Work Breakdown Structure presented previously. These new Subtask objectives are listed by Major Task and Task.

STATEMENT OF WORK - OPTIONAL TASKS

Major Task 1 - Improve Process Understanding & Capability

Task 1.1 Develop Process at Bench-Scale .

Subtask 1.1.5 Develop Advanced Mathematical Models: Current Alcoa computer models take an average or ensemble approach to predicting the trajectory, velocity and fraction solid of droplets arriving and interacting at the substrate and or deposit surface. More comprehensive models are required to look at individual droplet interactions in flight and at the deposit. Better models are also needed to predict droplet splashing vs. bouncing under various spraying and substrate conditions. The objective of this sub-task is to experimentally study the thermal state and impact behavior of alloy 6111 droplets under various droplet and deposit conditions. This data can then be used to develop more complex computer models.

Major Task 2 - Advanced Development Unit - Design and Construction

Task 2.1 Design the Advanced Spray Forming Development Unit

Subtask 2.1.8 Advanced Substrate Developments: The Advanced Development Unit, as designed in this revised proposal, will have no provisions for alternate material evaluation nor continuous product removal. As sprayed deposit size will be limited by the stainless steel substrate travel and the chamber size. The objectives of this subtask are to increase the versatility of the substrate module by incorporating equipment to overcome these deficiencies. All modules will continue to be designed to bolt to the chamber for easy replacement.

Sub-Subtask 2.1.8.1 Substrate Material Evaluation: This sub-subtask will investigate alternate substrate materials, coatings, and cooling methods appropriate for the production of 6111 automotive sheet. Substrate characteristics will be predetermined via computer and physical simulations, prior to evaluation in the ADU.

Sub-Subtask 2.1.8.2 Advanced Substrate Module(s): This sub-subtask will design, build and evaluate the use of gas seals in the chamber walls and belt substrates to provide for continuous product removal. This would enable longer ADU runs and deposits.

Subtask 2.1.9 Gas Recovery System: The gas delivery system on the Advanced Development Unit will be designed for once-through use of the atomizing gas. Alcoa believes that gas recycling will be necessary in commercial practice to achieve the full economic benefits of producing sheet via spray forming. The objective of this sub-task is to perform a paper study on a spent gas cleaning system and appropriate instrumentation and controls needed to properly recover the gas while meeting all local, state, and federal safety, health and environmental regulations. Cyclones or conventional filters are envisioned for the commercial unit. Design criteria, investment requirements, and operating costs will be estimated to form the basis for selection of an appropriate commercial system. This information will be later incorporated into the economic analysis.

Subtask 2.1.10 Overspray Recovery Module: With the use of the current wet-scrubbing system for operating the bench scale unit and the proposed ADU, no allowance is made for the recovery of fine overspray powders for analysis. The objective of this optional sub-task will be to design, purchase and install a cyclone and/or high capacity/high volume filter to capture dry overspray particulate for characterization.

Major Task 3 - Process/Product Development - ADU

Task 3.3 Produce/Evaluate 6111 Sheet

Subtask 3.3.4 Produce Additional Sheet Metal: Aluminum spray formed sheet will be produced only in sufficient quantity and size to meet product characterization sample requirements. Additional sheet sample production would be limited to quantities needed for Show & Tell presentations to potential material users and licensees to the Holding Company. The objective of this sub-task is to identify and produce a comprehensive quantity of sheet and formed parts for use in marketing the process and as test and evaluation (T/E) samples. Alcoa, with the appropriate DOE and automotive industry contacts, will establish the quantity and type of samples needed, and institute and manage the inventory.

Subtask 3.3.5 Advanced Product Characterization: Typical mechanical properties of interest to the Automotive industry include Ultimate Tensile Strength, Yield Strength, and %Elongation, in addition to basic formability data from the Guided Bend and Limited Dome Height tests. These provide a baseline for screening materials for further consideration. The objective of this sub-task is to expand the property database of Aluminum alloy 6111 spray formed sheet through specific tests methods of interest to automotive body sheet fabricators. These would include: Corrosion resistance, Weldability evaluation (both arc and spot), and the fabrication of specific shapes to evaluate Crushability.

ATTACHMENT II — TAFA SPRAY FORMING RUNS

Nozzle Type	# of Successful Runs	Pressure (psi) Nom Range	Gas/Metal Nom G/M Range	Spray Dist. (inches) Range	Substrate Type	Other - Nozzle Parameters, etc.
Alcoa I	3	45 40-50	0.6 0.24-1.2	26	0.5 in. Mild Steel	Varied liquid slit length to reduce melt flow rate.
USGA 4"	19	85 60-104	0.6 .24-1.2	13.5-22.5	0.5 in. steel 0.5 in. 304 SS Heated SS	Liquid, tip extension, asymmetric impingement angles, gas slit
USGA 8"	13	60 48-78	0.4 0.31-0.46	15-21	0.5 in. steel	Gas slit opening
Alcoa II	7	65 40-112	0.8 0.5-1.2	13-22	0.5 in. 304 SS	Liquid tip length, shroud
INEEL 2.6"	4	14 10-17	0.96 0.81-1.1	9-16	0.5 in. steel 0.5 in. 304 SS	Nozzle temp (1311 F - 1548)
Alcoa III	26	45 31-63	0.45	15.5-27	0.5 in. 304 SS Foil-coated Insulating Board	Gas slit width

ATTACHMENT II (cont.)

MARKO SPRAY FORMING RUNS

Nozzle Type	# of Runs	Pressure (psi) Nom Range	Spray Dist. (inches) Range	Other - Nozzle Parameters, etc.
UC-I *	20	245 180 - 265	15.75 - 18.00	Various alloys (3003, 6111) and Al-binaries (Zr, Cu, and Fe)
Circular Alcoa III	55	100 85 - 130	10.125 - 16.25	Varied liquid metal superheat, substrate material and grain refiner content to establish effect on porosity.

* Nozzle borrowed initially from the University of California - Irvine, to show feasibility of using the Marko unit as a spray forming research tool.

ATTACHMENT III — HISTORICAL BIBLIOGRAPHY OF COMPUTER MODELLING RESEARCH ON SPRAY FORMING

1989:

Gutierrez-Miravete, E., et. al., "A Mathematical Model of the Spray Deposition Process," *Metallurgical Transactions A*, Vol. 20A, pp. 71-85.

Unal, A., "Liquid Break-Up in Gas Atomization of Fine Aluminum Powders," *Metallurgical Transactions B*, Vol. 20B, pp. 61-69.

1990:

Bewlay, B. P., et al., "Modeling of Spray Deposition," *Metall. Trans. B*, Vol. 21B, No. 5, pp. 899-912.

1991:

Connelly, S., "An Investigation of Heat Transfer Phenomena in Spray Deposition Processes," Ph.D. thesis, Department of Mechanical Engineering, University College of Swansea, University of Wales.

Trapaga, G. and Szekely, J., "Mathematical Modeling of the Isothermal Impingement of Liquid Droplets in Spraying Process," *Metallurgical Trans. B*, Vol. 22B, pp. 901-913.

1992:

Ojha, S. N., "Spray Forming: Science and Technology," *Bull. Mater. Sci.*, Vol. 15, No. 6, pp. 527-542.

1993:

Grant, P. S., Cantor, B. and Katgerman, L., "Modeling of Droplet Dynamic and Thermal Histories During Spray Forming - I. Individual Droplet Behavior," *Acta Metall. Mater.*, Vol. 41, No. 11, pp. 3097-3108.

Grant, P. S., et al., "Modeling of Droplet Dynamic and Thermal History During Spray Forming-II. Effect of Process Parameters," *Acta Metall. Mater.*, Vol. 41, No. 11, pp. 3109-3118.

Leatham, A. G. and Lawley, A., "The Osprey Process: Principles and Applications," *Int. J. Powder Metallurgy*, Vol. 29, No. 4, pp. 321-329.

Liu, H., Lavernia, E. J., and Rangel, R. H., "Numerical Simulation of Substrate Impact and Freezing of Droplets in Plasma Spray Processes," *Journal of Physics D: Applied Physics*, Vol. 26, No. 11, pp. 1900-1908.

Liu, H., et al., "Numerical Simulation of Substrate Impact and Freezing of Droplets in Plasma Spray Processes," *J. Phys. D: Appl. Phys.*, Vol . 26, pp. 1900-1908.

Payne, R. D., et al., "Spray Forming Quality Predictions via Neural Networks," *J. Mater. Engr. Performance*, Vol. 2(5), pp. 693-701.

1994:

Cheng, C., et al., "Modeling-Based Microstructure Control in Spray Casting," Source unknown.

Fritching, U. and Bauckhage, K, "Spray Modeling in Spray Forming," FED-Vol. 201/HTD-Vol. 297, pp. 49-54, ASME.

Gethin, D. T., et al., "A Comparison of Lumped Parameter Numerical Techniques for Liquid Metal Sprays," Resource unknown.

Peaslee, K. D. and Robertson, G. C., "Modeling of Fluid and Particle Flow to Study Metal Powder Production Through Atomization," Paper presented in the TMS 1994 Annual Meeting, San Francisco, CA, March.

Solonenko, O. P., et al., "The Complex Study of Metal Drop-Substrate Interaction," *Proc. Int. Seminar ISECTA'93*, pp. 319-343, Almaty, Kazakhstan.

1998:

Cai, W. and Lavernia, E. J., "Modeling of Porosity during Spray Forming: Part I. Effects of Process Parameters," *Metallurgical and Materials Transactions B*, Vol. 29B, pp. 1085-1096.

Sprivastava, A. K., et al., "Microstructural Features and Heat Flow Analysis of Atomized and Spray-Formed Al-Fe-V-Si Alloy," *Metallurgical and Materials Transactions A*, Vol. 29A, pp. 2205-2219.

ATTACHMENT IV — METALS INITIATIVE HOLDING COMPANY AGREEMENT (DE - GM07 - 98ID11353)

THIS AGREEMENT, effective as of the 18th day of October, 1993 is entered into between the UNITED STATES OF AMERICA, (hereinafter referred to as "Government") as represented by the DEPARTMENT OF ENERGY (The DOE), and Aluminum Company of America (ALCOA) a corporation organized under the laws of the Commonwealth of Pennsylvania (the "Holding Company"), with its principal place of business located in Alcoa Center, PA.

WHEREAS, by Public Law 99-100, 99 STAT. 1253, Public Law 100-680, 102 STAT. 4073 and Public Law 101-121, 103 STAT. 731, Congress provided funding for a research and development initiative for new technologies to increase significantly the energy efficiency in the American metals industries (the "Metals Initiative");

WHEREAS, the DOE has, through various findings and determinations elected to waive title to inventions conceived for first actually reduced to practice under the Metals Initiative Program, including the Project as described in Spray Forming Aluminum and cooperative agreement DE-FC07-94ID13238, (the "Projects"), in order to further the purposes of the Metals Initiative; and

WHEREAS, the industry participants ("Industrial Participants"), have designated the Holding Company to be the entity to conduct on their behalf such activities as patenting, licensing, accounting, record keeping, and funds disbursing relating to inventions arising out of the Project.

NOW, THEREFORE, in consideration of the mutual covenants, conditions, and agreements herein contained, the parties hereto hereby agree as follows:

ARTICLE I - DEFINITIONS

I. Certain defined terms
As used in this Agreement, the following terms shall have the respective meanings indicated below, such meanings to be applicable equally to both singular or plural forms of such terms.

A. "Agreement" - This Agreement, as the same may be amended, supplemented or otherwise modified from time to time.

B. "Contracting Officer" - A person with the authority to enter into, administer and/or terminate contracts and agreements and make related determinations and finding on behalf of DOE.

C. "DOE" - U.S. Department of Energy.

D. "Government" - The United States of America.

E. "Gross Royalty Income" - All income, receipts, fees and proceeds of whatever kind received by the Holding Company from the licensing of each Project Invention, or any Protected Metals Initiative Project Data, and of any copyrighted data first produced in the performance of a contract specifically directed to and a part of the Project.

F. "Industrial Participant" - Those parties which have chosen to participate in the Project, as identified in Attachment A hereto, as may be amended to add additional parties.

G. "Net Royalty Income" - Gross Royalty Income less amounts for payment of costs associated with the preparation of patent applications, filing fees, prosecution costs, issue fees, maintenance fees, licensing expenses, and other directly associated costs of the administration of Project Inventions, unless otherwise provided by ARTICLE 8 hereof. Licensing costs include only the reasonable costs of direct salaries and travel expenses of personnel engaged in licensing activities and also include associated legal, accounting, and consulting costs. Travel expenses will be subject to the limitations contained in the Federal Acquisition Regulation (FAR) 31.205-46, in effect on the effective date of this Agreement.

H. "Patent Counsel" - The DOE Patent Counsel assisting the procuring activity.

I. "Project Inventions" - Subject inventions made under a contract specifically directed to and a part of the Project.

J. "Repayment Obligation" - An amount equal to 150 percent of the Government's total payments to the Project, which must be paid by the Holding Company to the DOE.

K. "Protected Metals Initiative Data" - Protected Metals Initiative Data produced under a contract specifically directed to and a part of the Project.

II. Cross References

The words "hereof," "herein," and "hereunder," and words of a similar impact, when used in this Agreement shall refer to this Agreement as a whole and not to any particular provision. Article and paragraph references are to Articles and paragraphs of this Agreement, unless otherwise specified.

ARTICLE 2 - INVENTIONS AND RELATED REQUIREMENTS

I. Invention Disclosures and Election of Title

A. When Patent Counsel determines that an invention which has been disclosed to Patent Counsel has been made under the above-identified DOE Metals Initiative Project and that a waiver of DOE rights applies by which title to such invention has been waived to the Holding Company as the designated holding company, DOE shall promptly forward to the Holding Company a full written disclosure of such Project Invention.

B. The Holding Company shall elect in writing whether or not to retain domestic title to any such Project Invention by notifying in writing Patent Counsel within six months of disclosure of the Project Invention to the Holding Company, or such longer period as may be authorized by Patent Counsel for good cause shown in writing by the Holding Company. However, in any instance where the Project Invention was described in a printed publication or was in public use or on sale such that the one-year statutory period wherein valid patent protection can still be obtained in the United States has been initiated, the period for election of title terminates sixty days prior to the end of the statutory period. With six (6) months of the Holding Company's written election the Holding Company will specify to Patent Counsel in writing those foreign countries, if any, in which foreign patent rights will be pursued on behalf of the Holding Company.

C. Subject to the provisions of this Agreement, with respect to a Project Invention, the domestic title to which has been elected to be retained by the Holding Company pursuant to Paragraph (A) (2) above, the Holding Company reserves the entire domestic right, title and interest in any United States patent application on the Project Invention filed, and any resulting United States Patent secured, by the Holding Company.

D. Subject to the provisions of this Agreement, with respect to a Project Invention, the foreign patent rights to which have been elected to be retained by the Holding Company in specified foreign countries pursuant to Paragraph (A) (2) above, the Holding Company reserves the entire right, title and interest in any foreign patent application on the Project Invention filed, and any resulting foreign patent secured, by the Holding Company in those foreign countries specified.

E. The waiver of rights in any Project Invention by the DOE shall be effective on the date the Holding Company's written election to retain the waived rights in that Project Invention is submitted to Patent Counsel.

II. Filing of Patent Applications

A. With respect to each Project Invention in which the Holding Company elects to retain domestic title pursuant to Paragraphs (A) (2) of this ARTICLE 2, the Holding Company shall have a domestic patent application filed on the Project Invention within six months after the waiver of right by the DOE has become effective with respect to that Project Invention or such longer period of time as may be approved by Patent Counsel for good cause shown in writing by the Holding Company. With respect to the Project Invention, the Holding Company shall promptly notify the Patent Counsel of any decision not to file an application.

B. For each Project Invention on which a domestic patent application is filed by the Holding Company, the Holding Company shall:

1. Within two months after the filing, deliver to Patent Counsel a copy of the application as filed, including the filing date and serial number;

2. Include the following statement in the second paragraph of the specification section of the application filed and any patents issued on a Project Invention: "The Government of the United States of America has rights in this invention pursuant to Contract (or Grant) No.__________ awarded by the U.S. Department of Energy";

3. Provide Patent Counsel with a copy of the patent within two months after a patent is issued on the application;

4. Not less than 30 days before the expiration of the response period for any action required by the United States Patent and Trademark Office, notify Patent Counsel of any decision not to continue prosecution of the application and deliver to Patent Counsel executed instruments granting the Government power of attorney;

5. Within six months after filing the application, deliver to the Patent Counsel a duly executed and approved instrument fully confirmatory of all rights to which the Government is entitled, and provide DOE an irrevocable power to inspect and make copies of the patent application filed.

C. With respect to each Project Invention in which the Holding company has elected pursuant to Paragraph (A) (2) of this ARTICLE 2 to retain the patent rights waived in specified foreign countries.

1. The Holding Company shall file a patent application on the Invention in each specified foreign country in accordance with applicable statutes and regulations within one of the following periods:

   a) Eight months from the date of filing a corresponding United States application, or if such an application is not filed, six months from the date the waiver has become effective with respect to that Invention;

   b) Six months from the data a license is granted by the Commissioner of Patents and Trademarks to file the foreign patent application where such filing has been prohibited by security reasons; or

   c) Such longer period as may be approved by the Patent Counsel for good cause shown in writing by the Holding Company.

2. The Holding Company shall notify the Patent Counsel promptly of each foreign application filed and upon written request shall furnish an English version of the application without additional compensation.

III. Terms and Conditions of Waived Rights

A. Subject to any licenses consistent with the requirements of ARTICLE 4 below, which the Holding Company may have granted in the Invention, the Holding Company agrees to convey to the Government, upon request, the entire domestic right, title and interest in any Project Invention when the Holding Company:

   1. Does not elect pursuant to Paragraph (A) (2) of this ARTICLE to retain such rights;

   2. Fails to have United States patent application filed on the Invention in accordance with Paragraph (B) (1) of this ARTICLE, or decides not to continue prosecution of such application; or

   3. At any time, no longer desires to retain title.

B. Subject to any licenses consistent with the requirement of ARTICLE 4 below, which the Holding Company may have granted in the Invention, the Holding Company agrees to convey to the Government, upon request, the entire right, title and interest in any Project Invention in any foreign country if the Holding Company:

1. Does not elect pursuant to Paragraph (A) (2) of this ARTICLE to retain such right in the country; or

2. Fails to have a patent application filed in the country on the Project Invention in accordance with Paragraph (B) (3) of this ARTICLE, or decides not to continue prosecution or to pay any maintenance fees covering the Invention. To avoid forfeiture of the patent application or patent, the Holding Company shall notify the Patent Counsel not less than 60 days before the expiration period for any action required by the foreign Patent Office.

C. Conveyances requested pursuant to Paragraphs (C) (1) and (C) (2) of this ARTICLE shall be made by delivering to the Patent Counsel duly executed instruments and such other papers as are deemed necessary to vest in the Government the entire right, title, and interest in the Project Invention to enable the Government to apply for and prosecute patent applications covering the Project Invention in this or the foreign country, respectively, or otherwise establish its ownership of the Project Invention.

D. For each Project Invention in which the Holding Company initially elects pursuant to (A) (2) of this ARTICLE not to retain the rights waived, the Holding Company shall inform the Patent Counsel promptly in writing of the date and identify of any on-sale, public use, or public disclosure of the invention which may constitute a statutory bar under 35 USC 102, which was authorized by or known to the Holding Company, or any contemplated action of this nature.

E. Government License
With respect to any Project Invention in which the Holding Company retains title, the Federal Government shall have a nonexclusive, nontransferable, irrevocable, paid-up license to practice or have practiced for or on behalf of the United States the Project Invention throughout the world.

ARTICLE 3 - MARCH-IN RIGHTS, ASSIGNMENT OF PAYMENTS, DEFAULT AND TERMINATIONS

I. The Holding Company agrees that with respect to any Project Invention in which it elects to retain title, the DOE has the right in accordance with the procedures in 37 CFR 401.6 and any supplemental regulations of the DOE to require the Holding Company, an assignee, or an exclusive licensee of a Project Invention to grant a nonexclusive, partially exclusive, or exclusive license in any field of use to a responsible applicant or applicants, upon terms that are reasonable under the circumstances, and if the Holding Company, assignee, or exclusive licensee refuses such a request, the DOE has the right to grant such a license itself if the DOE determines that:

A. Such action is necessary because the Holding Company or assignee has not taken, or is not expected to take within a reasonable time, effective steps to achieve practical application of the Project Invention in such field of use;

B. Such action is necessary to alleviate health or safety needs that are not reasonably satisfied by the Holding Company, the assignee, or their licensees;

C. Such action is necessary to meet requirements for public use specified by federal regulations and such requirements are not reasonably satisfied by the Holding Company, the assignee, or their licensees; or

D. Such action is necessary because the licensing contemplated by ARTICLE 4 of this Agreement has not <u>commenced</u> or because the Holding Company is in <u>material</u> breach of the licensee's agreement with the Holding Company.

II. Should the Holding Company be in default or in breach of any provisions of this Agreement, and if such <u>material</u> breach shall continue for 30 days following written notice thereof by the DOE to the Holding Company, the DOE shall have the right, in addition to any other rights in law or equity, to declare this Agreement to be ended and have no further obligation to the Holding Company under this or any related agreement, and with respect to any license or assignment under which proceeds or royalty payments are due the Holding Company, to direct any such licensee or assignee to make all further remittances directly to the DOE and release said licensee or assignee from any further obligation to the Holding Company <u>excluding confidentiality obligations</u>.

III. Any waiver of the right retained in accordance with ARTICLE 2, Paragraphs (A) (2), (A) (3), and (A) (4), as applied to particular Project Inventions may be terminated at the discretion of the Secretary of Energy or his designee, in whole or in part, if the Holding Company fails to comply with the provisions set forth in ARTICLE 2, Paragraphs (B) and (C), and ARTICLES 4, 5, 6, 7, 9, and 10 and such failure is determined by the Secretary of Energy or his designee to be material and detrimental to the interest of the United States and the general public. Prior to terminating any waiver of rights, the Holding Company will be given written notice of the intention to terminate the waiver of rights, the extent of such proposed termination and the reasons therefor, and a period of 30 days, or such longer period as the Secretary of Energy or his designee shall determine for good cause shown in writing, to show cause why the waiver of rights should not be so terminated.

ARTICLE 4 - LICENSING ACTIVITIES

I. With respect to each Project Invention for which the Holding Company elects to retain title as provided in ARTICLE 2 above, the Holding Company shall enter into license agreements with Industrial Participants and others who are not Industrial Participants consistent with the following requirements:

A. Royalty-Free License to Industrial Participants
Subject to ARTICLE 6, the Holding Company shall grant to each Industrial Participant, upon the written request of such Industrial Participant, a royalty-free, nonexclusive license in any Project Invention. The license shall expressly preclude sublicensing by the Industrial Participant. The license shall require that any products sold in the United States be manufactured substantially in the United States.

B. Royalty-Bearing Licenses to Others
The Holding Company shall also make good faith efforts to license Project Inventions to others who are not Industrial Participants on reasonable terms and conditions and at reasonable royalty rates based upon the volume or selling price of products produced with the use of such Project Inventions or upon any other commercially reasonable basis for establishing royalty rates. Any such license in a Project Invention shall be royalty-bearing and nonexclusive, shall expressly preclude sublicensing and shall require that any products sold in the United States be manufactured substantially in the United States. In addition, the royalties assessed a non-Industrial Participant licensee shall be on a basis that will be beneficial and equitable to the Industrial Participants. In determining the total royalty to be assessed, consideration shall be given to American companies that are substantially involved in the U.S. domestic production of metals and related manufacturing processes.

II. The Holding Company reserves the right to license Project Inventions to U.S. and non-U.S. concerns for use both in the United States and in foreign countries, provided that the products developed and manufactured in foreign countries do not compete unfairly with products developed and manufactured in the United States.

III. Any licenses granted to non-U.S. concerns will be subject to all the requirements set forth in Paragraph (A) (2) of this ARTICLE 4.

IV. Appropriately marked Protected Metals Initiative Project Data shall be made available, and a copy delivered, to the Holding Company. Although Protected Metals Initiative Project Data shall be made available to the Industrial Participants in the DOE Metals Initiative Project for their use in performing work or monitoring progress under the Project and for their use in utilizing and commercializing the technology being developed under the Project, the Industrial Participants shall be subject to the restrictions on disclosure, publication, and dissemination contained in the markings, and are not accorded a right to license such Data. The Holding Company shall have the right, and shall make good faith efforts, to license such Protected Metals Initiative Project Data or include such Protected Metals Initiative Project Data in a license with other technology developed under the Metals Initiative Projects. Such licenses shall include appropriate provisions, including obligations of confidentiality and reasonable royalty rates, so as to benefit the Industrial Participants of the Metals Initiative Project. In licensing Protected Metals Initiative Project Data, the Holding Company is also subject to the requirements and obligations which apply to the licensing of Project Inventions as set out in ARTICLE 4, Paragraphs (A) (2), (B), and (C), ARTICLE 5, and ARTICLE 6.

V. In licensing Project Inventions and Protected Metals Initiative Project Data, the Holding Company shall be responsible for compliance with applicable export control laws.

ARTICLE 5 - PROHIBITION AGAINST EXCLUSIVE LICENSES AND ASSIGNMENT

The Holding Company agrees that it will not grant to any party the exclusive right to use or sell any Project Invention or license such use in the United States or in foreign countries. Notwithstanding the provisions of Paragraph (A) (1) of ARTICLE 4 above, any exclusive license shall provide for royalty payments in accordance with Paragraph (A) (2) of ARTICLE 4. The Holding Company agrees that it will not assign title to any Project Invention without the approval of Patent Counsel.

ARTICLE 6 - REPAYMENT OF GOVERNMENT CONTRIBUTIONS

I. In order to assist in satisfying the Congressionally required repayment to the Federal Government of 150 percent of the Government's expenditures under this Project from the proceeds of the commercial sale, lease, manufacture, or use of technology developed under the Project, at a rate of one-fourth of all Net Royalty Income, each license agreement with an Industrial Participant shall require the Industrial Participant to pay to the Holding Company a fee ("Participant's Fee) equal to 25 percent of the royalty rate established for non-participants with respect to the Project's technology being licensed, such Participant's Fee to be payable only until the Government Repayment Obligation hereinafter referred to shall have been satisfied. The Holding Company shall treat all Industrial Participants' Fees received by it as "Gross Royalty Income." If, three (3) years after completion or termination of the Project under the Industrial Participants' contracts to carry out the Project, the Holding Company has not issued a license to a non-participant so as to establish a royalty-rate to determine the appropriate Participant's Fee, the Holding Company agrees to negotiate in good faith with DOE to determine an appropriate amount or rate for the Participant's Fee.

II. The Holding Company shall pay monthly to DOE 25 percent of net Royalty Income until the total of all such payments equals 150 percent of the Government's total payments to the Project (the "Repayment Obligation").

ARTICLE 7- DISTRIBUTION OF REMAINING NET ROYALTY INCOME

After payment of 25 percent of net Royalty Income to DOE under ARTICLE 6 above, the remaining Net Royalty Income shall be dealt with as shall be agreed by the Holding Company and the Industrial Participants.

ARTICLE 8 - PATENTING COSTS

The Holding Company agrees to bear all costs associated with the patenting of the Project Inventions for which it elects to retain title, including costs associated with the preparation of patent applications, filing fees, prosecutions costs, issue fees, maintenance fees and licensing expenses. To the extent that such costs paid by the Holding Company have not been included as part of any Industrial Participant's cost-sharing contribution to the Project, such costs will be deducted from Gross Royalty Income in determining Net Royalty Income. However, if such costs have been included as part of an Industrial Participant's cost-sharing contribution, the Holding Company may not deduct such amounts from Gross Royalty Income in determining Net Royalty Income.

ARTICLE 9 - REPORTING ON UTILIZATION OF PROJECT INVENTIONS

The Holding Company agrees to submit reports annually to the DOE on the utilization of project Inventions or on efforts at obtaining such utilization that are being made by the Holding Company of its licensees. Such reports shall include information regarding the status of development and date of first commercial sale or use and will provide an accounting for royalties received by the Holding Company, expenditures on account of each Project Invention, Holding Company costs, inventor awards, and such other data and information as is necessary to properly account for receipts and expenditures relating to Project Inventions. The Holding Company also agrees to provide additional reports as may be requested by the DOE in connection with any march-in proceeding undertaken by the DOE in accordance with ARTICLE 3. To the extent data or information supplied under this ARTICLE is considered by the Holding Company or its licensee to be privileged and confidential and is so marked, the DOE agrees that, to the extend permitted by 35 USC 202 (c) (5), it will not disclose such information to persons outside the Government.

ARTICLE 10 - AUDIT AND RECORDS

The Contracting Officer or representatives of the Contracting Officer shall have the right to examine and audit books, records, documents and other evidence and accounting procedures and practices, sufficient to reflect properly all costs claimed to have been incurred or anticipated to be incurred in performing this Agreement and all remittances or payments received (including amounts due but unpaid) for activities under this Agreement. This right of examination shall include inspection at all reasonable time of the Holding Company's offices, or parts of them, engaged in performing this Agreement. Since the Holding Company is required to furnish cost, funding or performance reports, the Contracting Officer or duly authorized representatives of the Contracting Office who are employees of the Government shall have the right to examine and audit books, records, other documents and supporting materials, for the purpose of evaluating (i) the effectiveness of the Holding Company's policies and procedures to produce data compatible with objectives of these reports and (ii) the data reported.

The Holding Company shall make available at its office during regular business hours the material described in the ARTICLE 10 for examination, audit or reproduction, until three years after expiration of any patents reserved by the Holding Company under this Agreement or for any longer period required by statute or by other clauses of this Agreement.

ARTICLE 11 - TERM OF AGREEMENT

The Agreement shall become effective on October 18, 1993, and shall continue until the expiration of all patents held by the Holding Company on elected Project Inventions or until all royalty or other payments are received by the Holding Company and disbursed and accounted for as required by this Agreement, whichever is later.

ARTICLE 12 - NOTICES

Whenever any notice is required or permitted to be given under any provisions of this Agreement, such notice shall be in writing, signed by or on behalf of the part giving the notice, and shall be deemed to have been duly given if personally delivered or sent by United States mail, overnight delivery service, or by telegraph, telex or facsimile transmission confirmed by letter and will be deemed given, unless earlier received (i) if sent by certified or registered mail, return receipt requested, or by first class mail, three (3) calendar days after being deposited in the United States mails, postage prepared, (ii) if sent by overnight delivery service, two (2) calendar days after being deposited with such service, (iii) if sent by telegram, telex or facsimile transmission, on the date sent, provided confirmatory notice is sent by first class mail, postage prepaid, and (iv) if delivered by hand, on the date of receipt. Such notice shall be addressed as set forth below to the party or parties to whom such notice is to be given (or at such other address as shall be stated in a notice similarly given):

(A) If to the DOE:

U.S. Department of Energy
Idaho Operations Office
Contract Management Division
785 DOE Place
Idaho Falls, ID 83401-1562

Copy to:

U.S. Department of Energy
Chicago Operations Office
Intellectual Property Law Division
9800 South Cass Avenue
Argonne, IL 60439

(B) If to the Holding Company:

Aluminum Company of America (ALCOA)
Alcoa Technical Center
100 Technical Drive
Alcoa Center, PA 15069-0001
ATTN: Government Operations

ARTICLE 13 - OFFICIALS NOT TO BENEFIT

No member of or delegate to Congress, or resident commissioner, shall be admitted to any share or part of this contract, or to any benefit arising from it. However, this clause does not apply to this contract to the extent that this contract is made with a corporation for the corporation's general benefit.

IN WITNESS WHEREOF, the parties hereto have executed this Agreement.

UNITED STATES OF AMERICA

BY: ____________________
David R. Williams
Aluminum Company of America
Contracting Officer

BY:
____
Contracting Officer

____
____
Date

ATTACHMENT A[3]

Industrial Participants

Aluminum Company of America (ALCOA) and any subsidiaries and affiliates thereof, in which ALCOA owns a 50% or greater interest.

Air Products and Chemicals, Inc. and any subsidiaries and affiliates thereof, in which Air Products and Chemicals, Inc. owns a 50% or greater interest.

---

[3] In 1998 Air Products withdrew its participation as an Industrial Participant.