YEARLY PROGRESS REPORT

Project Title: Reduction of Oxidative Melt Loss of Aluminum and Its Alloys

Covering Period: April 1, 2001 through March 31, 2002

Date of Report: July 7, 2002

Recipient: Secat, Inc.,
1505 Bull Lea Road
Coldstream Research Campus
Lexington, KY 40511

Award Number: DE-FC07-00ID13898

Subcontractors: University of Kentucky
Argonne National Laboratory
Oak Ridge National Laboratory
Albany Research Center

Other Partners: Alcan Aluminum Corp.
ARCO Aluminum, Inc.
Century Aluminum of Kentucky
Commonwealth Aluminum
Hydro Aluminum Louisville, Inc.
IMCO Recycling
Logan Aluminum
McCook Metals, LLC

Contact: Subodh Das, (859) 514-4955, skdas@engr.uky.edu

Project Team: DOE-HQ contact: Sara Dillich
DOE-Idaho contact: John Yankeelov
Industry contact: Subodh Das

Project Objective:

The project goal is to reduce melt loss during aluminum melting by 50%. To that end, the project objectives are to (1) develop an understanding of the key factors that contribute to the oxidation of molten aluminum, (2) determine the effects of major variables on the formation of dross during heating, melting, and holding of the melt at temperature, and (3) develop and evaluate technology that will reduce melt loss.

Background:

Fabrication of aluminum product requires melting and re-melting of aluminum metal and alloys. During the melting process, aluminum reacts with the furnace atmosphere and oxidizes, forming an aluminum-oxide-rich surface layer called dross. Approximately 480,000 tons of aluminum metal is lost to oxidation during the melting process. Achieving the project goal of preventing half of this melt loss would result in significant energy, environmental, and economic benefits for the domestic aluminum industry and the nation.

Literature suggests that the initial oxidation of molten aluminum is slow as the alumina forms a thin dross layer. This is often referred to as 2-dimensional oxide growth. After an initial incubation period, the oxidation rate of aluminum accelerates and a thick dross layer begins to form. This is often referred to as 3-dimensional oxide growth. If the transition from slow 2-dimensional oxide growth to rapid 3-dimensional oxide growth could be understood, technology could be developed to delay the onset of 3-dimensional oxide growth until the melt cycle is complete. Implementation of such technology is the goal of the project.

An internal quarterly project review meeting was held on March 20, 2002. One of the key action items that came out of the meeting was the need to reorganize the project along the seven concepts that are being developed for implementation to reduce melt loss. The project had been organized along Tasks designated for particular institutions (National Labs, University of Kentucky, Secat, and Industrial Partners). The new organization structure should help streamline the project and keep it focused on technology development and implementation. Because the work itself has not changed, milestones are still reported by Task.

Seven distinct concepts for reducing melt loss by delaying the onset of 3-dimensional growth in the dross layer of aluminum alloys are being pursued. The concepts are not mutually exclusive: implementation of any one concept will provide benefits that are increased when more than one concept is implemented. In some cases, all seven concepts could be implemented. The concepts are:

1. Alter furnace atmosphere
2. Alter melt chemistry
3. Reduce melt exposure
4. Proprietary – reduce oxidation on solid
5. Proprietary
6. Reduce surface temperature
7. Alter practice

The first three of these concepts are described in the proposal. The first two concepts, (1) altering furnace atmosphere and (2) altering melt chemistry, aim to cause chemical changes in the oxide layer that would prevent rapid 3-dimensional oxidation. The third concept aims to reduce oxidation by placing a solid barrier on the melt surface that would prevent oxygen in the furnace atmosphere from reaching the molten aluminum surface. The remaining four concepts were identified and developed during the project.

Status Summary:

This project began April 1, 2000. Eight alloys, one from each industrial partner, are being examined. Dross samples from each alloy have been collected and characterized at Oak Ridge. Based on these observations, a general model of aluminum alloy oxidation in industrial furnaces has been developed. Facilities and equipment to investigate the fundamentals of dross formation have been designed and constructed. These include the X-ray photoelectron spectroscope (XPS), the X-ray diffraction (XRD) furnace for in-situ measurement of the oxide structure growing on the molten metal sample using the Advanced Photon Source (APS) at Argonne, the solid-state NMR unit at the University of Kentucky, and the gas-fired reverberatory furnace at Albany.

Fundamental and applied research efforts are continuing. At Argonne, work focused on preparing a furnace set-up for in-situ monitoring of the 2-D to 3-D transition in the oxide growth rate using the Advanced Photon Source (APS). Two sets of experiments at APS to aid in this effort were performed: June 11-18 and November 26 – December 3, 2001. On the first two concepts, analysis of the data collected during the APS experiments in December 2001 began. Software to analyze the data was developed. The experimental work at the APS identified a new parameter that affects dross formation. A way of implementing the result (Concept 5) is being developed. Additionally, the furnace used for APS studies was redesigned to allow for simultaneous XRD and X-ray Fluorescence (XRF) in-situ measurements of the oxide growing on molten metal, so that both chemical and structure data of the surface oxide can be collected. An XRF unit that has been designed is being manufactured. Compatibility studies to identify a suitable material to act as a solid physical barrier between the atmosphere and the melt have begun (Concept 3). Preliminary results indicated that a surface barrier could be used successfully to reduce dross formation. The University of Kentucky completed the coal-pyrite study model study and is relating the results to preventing spinel formation in dross. Solid-state NMR experiments to understand Mg-B interactions have begun. A new concept (Concept 4) has been identified as a way to reduce dross. Comparison between industrial and lab-generated dross has begun. Three metal samples were melted at Argonne under different conditions. Analysis is on going at Oak Ridge, but preliminary observations suggest that dross formation rate is much more dependant on melt temperature than previously thought. Ideas on implementing this result (Concept 6) are on going. Initial experiments using XPS and APS have suggested that the transition from 2-dimensional to 3-dimensional oxide growth can be controlled. Albany began melting trials to condition their mini gas-fired reverberatory furnace in preparation for experiments evaluating project concepts.

The project was initially monitored by Task. Project progress by task is outlined below in detail.

Detailed Progress on Tasks (Year 2: April 1, 2001 to March 31, 2002):

<u>Task 1. Sampling Protocols (All)</u>

–*Establish sampling procedures, tagging methods, archival storage, and web-based access to sample information*

Three members of the project team visited the last of the industrial partners' plants, Hydro Aluminum in Henderson, Kentucky, on June 1, 2001. The team met with Todd Johnson, Managing Director for Hydro Aluminum Henderson, to discuss the project, view operations, and discuss dross sampling methods and protocol. Also, the set-up of a secure web site was completed. The web site allows the project team members access to project information, status, and generated data. The web site is updated on a regular basis, usually weekly. This task is complete except for the need to maintain the project web site.

Task 2. Standard Alloys (Secat member companies)

–Prepare and collect industrial alloy standard materials for testing

The project team collected prime aluminum dross and metal samples from Hydro Aluminum Henderson. These samples were shipped to Oak Ridge National Laboratory for analysis of the dross layer. Additionally, 670 lbs of 3004 and 440 lbs of 5182 alloys were sent from Logan to Albany Research Center for melting experiments to be performed under Task 10. Logan provided 20 pounds of 3004-alloy to Argonne for testing under Tasks 5 and 6. Century provided Argonne with samples containing varying amount of Na and Li for testing under Task 8. Logan also provided Argonne with standard OES samples for use as benchmarks in Task 8 work. Commonwealth Aluminum provided approximately 200 pounds of 5052 scrap to Argonne for Task 9. Century Aluminum will also supply about 200 pounds of prime for Task 9. Effort remaining on this task is to collect a second set of dross and metal samples from the industrial partners' plants. The second set of samples will focus on specifics identified in the first set of samples that require further investigation. Discussion amongst the project team members suggested there was no need to collect a second complete set of metal and dross samples from the project partners. It was decided that a new set of metal and dross samples was required from Commonwealth, IMCO, Alcan-Berea, and Logan. The dross samples from Commonwealth will be collected and analyzed as a function of scrap type charged. Samples from IMCO and Alcan-Berea will be collected from the main hearth of the side-well furnaces at earlier process times to resolves some issues associated with sample variability and morphology of the oxide in those samples.

Task 3. Alloy Characterization (Argonne)

–Characterize alloy samples for both average composition and sample variability

Composition analysis is available for 6 of the 8 sample compositions. However, to get a better representation of minor and tramp element concentrations, it was decided to have the metal samples analyzed by glow discharge mass spectroscopy (GDMS). Glow discharge mass spectroscopy (GDMS) was used to determine the concentration of tramp and minor elements in 6 of the 8 metal samples – analyses of the remaining samples are scheduled for the next quarter. Results of the analyses provided detailed information on the concentration of tramp and minor elements in the various aluminum alloys, which will be used with Task 8 results to understand the effects of these elements on dross formation.

Task 4. Dross Sample Analysis (Oak Ridge)

–Analyze dross specimens from actual industrial melting processes

ORNL has received Al-dross samples from all the industrial participants. The dross was collected during individual plant visits using similar procedures at each plant in order to directly compare and contrast the microstructure and microchemistry of the different types of dross. Each sample was collected with a ladle using a “scooping” motion below the dross layer in order to collect liquid alloy plus the surface dross layer with minimal disturbance. Once received at ORNL, the bulk dross specimen was sectioned through the surface layer into the pure metal alloy. Samples were prepared from different areas of the dross layer. Micro structural characterization has been conducted on all of the industrial dross using electron microprobe analysis, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Extensive analysis has been conducted at ORNL thus far on dross samples received from

IMCO Recycling (3004 precursor), Logan (3004), ARCO/Logan (5182), Century (1350), McCook Metals (7075), Alcan-Berea (3104) and Hydro Aluminum (6063), and comparing them to the previously analyzed dross samples. It appears that all but one of the dross samples have similar layered structures. This pattern is evident in all the samples except the 5052. In the 5052 sample, the extent of pre-existing oxide and/or scrap charge appears to mask the dross evolution pattern. Analysis of the next set of samples including 5052 will occur during the summer of 2002.

Task 5. Oxidation Kinetics (Argonne)

–*Use APS to determine the effects of furnace atmosphere on oxide formation kinetics*

–*Construct hot-plate x-ray photoelectron spectroscopy (XPS) unit to look at the initial stages of aluminum alloy oxidation*

–*Increase number of experiments to look at all alloys*

The first x-ray diffraction experiments held at APS on June 11-18, 2001, provided information on the film structure on molten aluminum and aluminum alloy samples. More importantly, they indicated that these experiments are capable of providing the necessary data to determine the effects of furnace atmosphere on oxide formation kinetics. Prior to the experiments, two heating chambers were designed, built, and tested. Two types of x-ray techniques were evaluated with our experimental set-up: reflectivity and diffraction. The reflectivity experiments could provide information on the film surface and interfacial roughness, as well as film thickness. Data was collected continuously as the sample was allowed to oxidize at various temperatures and atmospheric conditions. The data indicated that the film surface and metal/film interface were too rough and that the film was too thin to yield useful information using x-rays. This applied to both solid and liquid samples. Therefore, a laser reflectivity apparatus has been assembled and is being evaluated for high-temperature measurements of the oxide films. The diffraction experiments performed at APS could provide information on the film structure. Because the films are relatively thin, a grazing angle incidence beam setup was used to insure a greater fraction of the diffracted beam originated from the specimen surface (see Figure 1). Data was collected continuously for aluminum, magnesium, and six alloys as a function of temperature and furnace chamber atmosphere. Analyses indicate that the surface films are primarily amorphous alumina, at least on the time scales we investigated (up to 3 hours). Results indicate that this technique is useful in providing the necessary data of film structure as a function of sample composition.

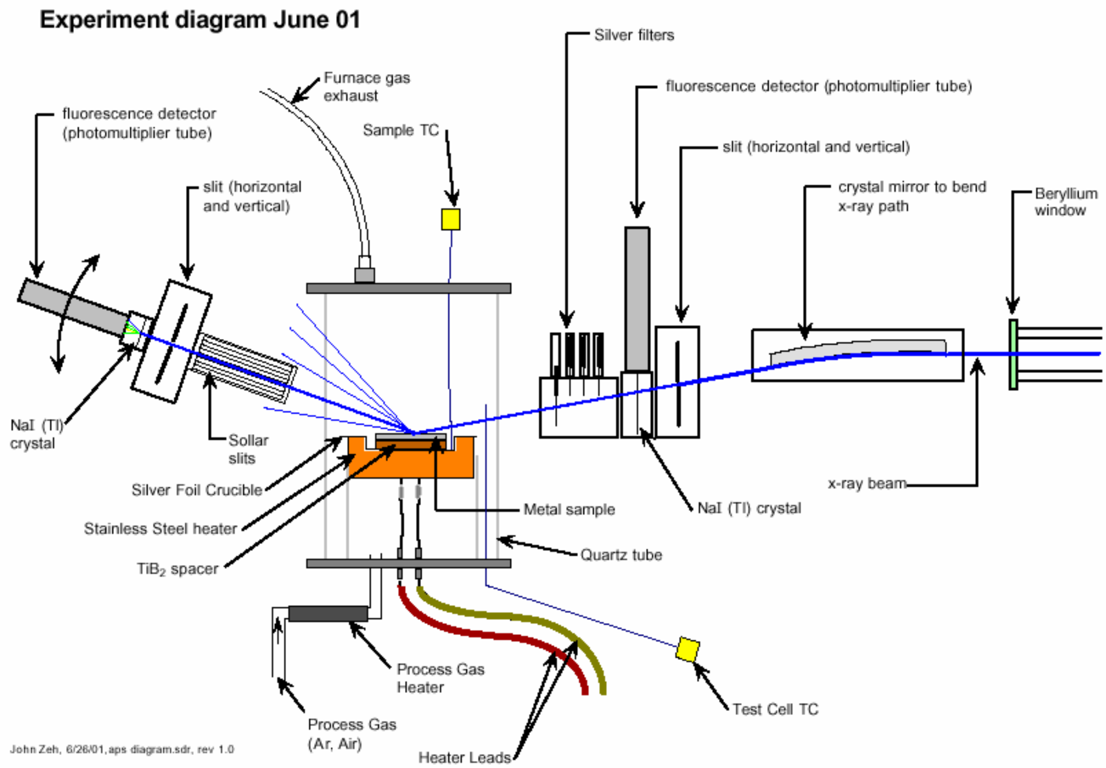


Figure 1. Schematic - grazing angle x-ray diffraction experimental setup at APS, June 11-18, 2001. Courtesy. John Zeh, Logan Aluminum.

A second set of experiments to determine the structure of the oxide formed during the initial stages of aluminum alloy oxidation were performed at the Advanced Photon Source November 26 to December 2, 2001. Several improvements where made to the x-ray diffraction experimental set-up, including the use of an image plate for faster data collection, and an improved sample mount. Grazing-incidence x-ray diffraction, a technique used during the first experiments at APS in June 2001, was again used to determine the crystal structure of the initial oxide that forms. A manual scraping technique was found to be an acceptable method of drossing the aluminum samples producing a clean molten metal surface on which new oxide could grow. Five alloys were tested – pure Al, 3004, 3104, 5052, and 5182. Analysis of the data is ongoing.

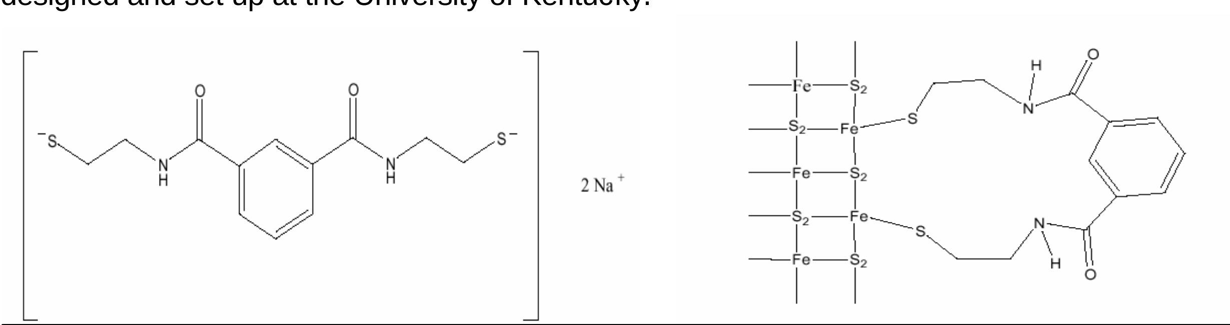
<u>Task 6. Dross Comparisons (Oak Ridge)</u>

–Compare lab-generated dross composition and structure with the industrial samples.

Metal/dross specimens from Argonne generated during the first set of APS experiments that were received at ORNL were not analyzed because the oxidation process was determined to be inadequate. Instead, 3004 alloy samples were melted and oxidized at 700 and 900°C at Argonne. Half the samples were drossed to determine the effect of pre-existing oxide on the dross growth rate. Analyses have not yet begun, but preliminary observation suggests that temperature plays a key role in dross formation, much greater than expected. Drossed samples held at 700°C appeared not to oxidize further. Analysis is ongoing.

Task 7. Growth Mode (Argonne and UK)
–Investigate the transition from 2-dimensional to 3-dimensional dross growth
–Investigate Mg-B interactions

Literature suggests that spinel formation might be a significant factor that affects the dross generation rate. As a result, a fundamental study by the University of Kentucky on the mechanics of spinel formation was added to this task. Preliminary work at the University of Kentucky was aimed at exploring whether additives attach to the surface of the periclase crystallites (MgO) thus preventing subsequent spinel formation ($MgAl_2O_4$). Short-term projects, which could help verify the role of additives in preventing periclase conversion, were designed. It was decided to explore whether the dissolution of sulfide minerals such as pyrite may be prevented by the addition of small amounts of sulfide compounds in aqueous systems at room temperature. The results of the experiments indicated that the addition of the disodium salt of 1,3-benzenediamidoethanthiol ($BDETNa_2$) (Figure 2A), a compound that had been previously shown to bind Fe^{+2} as well as other metals, substantially prevented the leaching rate of pyrite in coal. It is postulated that the terminal sulfur groups covalently coordinate to the lattice of the ferrous atom in the cubic structure of pyrite (Figure 2B). It is thought that the results form this set of experiments support the idea that additives may behave similarly in preventing the conversion of periclase to spinel. Experiments to test this hypothesis are currently being designed and set up at the University of Kentucky.



A B

Figure 2. A – structure of $BDETNa_2$. B – Theoretical schematic of $BDETNa_2$ covalently bound to the pyrite surface.

Task 8. Alternative Dopants (Argonne and UK)
–Investigate variables for specific alloys that have a large effect on dross growth rate (minor and tramp elements) (Argonne)
–Investigate B effects with NMR facilities (UK)

At Argonne, a series of XPS experiments are planned to determine the growth rate of oxides as a function of minor and impurity element concentrations. Specimens were obtained from Logan and Century. Additional staff to perform this task has been identified and should be joining the research team in the near future.

At UK, oxide specimens containing combinations of MgO and B_2O_3 at ratios from 1 to 10,000 have been examined at temperatures between 600° and 1000°C. X-ray diffraction of the solid oxide specimens indicates the presence of unidentified peaks, which might be the hypothesized MgO-boron compounds that prevent spinel formation. Experiments using solid-state NMR techniques should provide enough detail to identify these compounds.

Task 9. Melt Exposure (Argonne)

–Determine the effect of decreasing the melt exposure to atmosphere on oxide growth transition

Several materials have been identified that could decrease melt exposure to the atmosphere and limit dross formation. An experimental set-up was prepared. Source metal to be provided by the industrial partners was identified. Several candidate materials were identified based on density, thermal conductivity, and minimal reaction with molten aluminum. Several materials were tested in molten aluminum at temperatures ranging from 660°C to 900°C for times from 30 min to 1 hr. Of the materials tested, one showed the least amount of reaction with molten aluminum.

Task 10. Agitation and Solid Oxidation Effects (Albany)

–Design and construct/re-line pilot gas-fired furnace

–Determine effect of alloy form and stirring on dross formation

–Investigate effects of solid oxidation including ingot burning

Activities in Task 1 identified a need to expand this task to include an investigation of solid aluminum oxidation during heat-up and the significance of this effect on overall dross formation. Experiments in this task will be performed in a 200-lb-gas-fired furnace that has been designed specifically for this task. The furnace has been assembled and refractories have been cured. The door and damper/exhaust assembly are being manufactured. Scrap aluminum from Logan for pre-melting tests has been received. The effort has been delayed due to the installation of more-advanced furnace instrumentation. This is a 175-200 lb furnace equipped with a Maxon Ramfire burner of 50,000 to 800,000 Btu capacity. The refractory lining is 70% alumina. Instrumentation for melt, plenum, exhaust and shell temperatures, furnace pressure, CO/CO_2 levels, gas consumption and flow rate has been installed. However, necessary load cells to weigh the furnace and determine the dross growth rate as a function of different variables have not yet been installed. Pre-melting trials are underway to condition the refractories. The furnace is expected to be completed and ready for experiments in the spring of 2002.

Task 11. Scale –up (Secat)

–Use industrial melt-furnace trials to validate dross limitation steps

No progress – no effort scheduled for this period.

Task 12. Modeling (Oak Ridge)

–Model element partitioning during melting and oxidation of aluminum laboratory experiments and industrial furnaces

An aluminum oxidation hierarchy continued to be supported by experiments. In addition, results suggest that surface temperature of molten metal is more significant for dross formation that previously thought. The current model supports the formation of aluminum nitrides and oxynitrides. Experiments are being planned at Argonne to test the model with respect to nitrides, oxynitrides, and temperature.

Task 13. Project Report (All)

This task addresses meeting and reporting requirements. The first annual project review meeting was held April 19, 2001, and the presentations from that meeting were included in the annual report for the period. April 1, 2000, to March 31, 2001. Project review meetings were held August 15, 2001, Dec. 12, 2001, and March 20, 2002. Additionally, a DOE review was held October 17, 2001.

Plans for Next Year:

Plans for the third and final year of the project include preparation for APS experiments at Argonne, scheduled for June 26 – July 8, 2002, for Task 5 and 7 work in support of Concepts 1, 2, 5, and 6. Bench-scale experiments are planned at Argonne as part of Task 8 and 9 in support of Concepts 3, 4, 5, and 6. Experiments at Albany are planned as part of Task 10 in support of Concepts 4 and 7. Dross characterization at Oak Ridge will support Concept 7 (Task 4) and Concepts 3, 4, 5, 6, and 7 (Task 6). University of Kentucky will perform experiments in fundamental science to support Concepts 2 and 4 (Tasks 7 and 8). The industrial partners will: (1 – ARCO) provide material for Concept 4 testing at Albany, (2 – Commonwealth) prepare melts to characterize dross in support of Concept 7, (3 – Logan) collect dross samples in support of Concept 7, (4 – Hydro) provide proprietary industrial data in support of Concept 4, and (5 – all) collect metal samples in support of Concept 5 (Tasks 2 and 3). Pilot-scale tests of the most promising concept will be performed in the second half of the year.

Patents: Nil through March 31, 2002 resulting from this award.

Milestone Status Table: (as of March 31, 2002). Schedule revised on 3/18/01 to coincide with dates based on the Secat CRADA with the three National Labs. Detailed progress is monitored on a Gantt chart.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Sample Protocol	6/2/03		89% done
2	Standard Alloys	4/2/02		27% done
3	Alloy Characterization	5/28/02		38% done
4	Dross Sample Analysis	10/29/02		58% done
5	Oxidation Kinetics	9/17/02		66% done
6	Dross Comparison	12/10/02		28% done
7	Growth Mode	12/20/02		50% done
8	Alternative Dopants	12/20/02		33% done
9	Melt Exposure	10/25/02		75% done
10	Melt Agitation and Solid Effects	1/3/03		56% done
11	Scale-up	5/23/03		1/6/03 start date
12	Modeling	12/20/02		50% done
13	Final Report	6/26/03		

Budget Data (as of date): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

Excel spreadsheet enclosed