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Liquid Metal Processing and Casting Experiences at the US Department of Energy's Albany Research Center

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Abstract

In this paper we will discuss some of the early pioneering work as well as some of our more recent research. The Albany Research Center (ARC) has been involved with the melting and processing of metals since it was established in 1942. In the early days, hardly anything was known about melting refractory or reactive metals and as such, virtually everything had to be developed in-house. Besides the more common induction heated air-melt furnaces, ARC has built and/or utilized a wide variety of furnaces including vacuum arc remelt ingot and casting furnaces, cold wall induction furnaces, electric arc furnaces, cupola furnaces and reverberatory furnaces. The melt size of these furnaces range from several grams to a ton or more. We have used these furnaces to formulate custom alloys for wrought applications as well as for such casting techniques as spin casting, investment casting and lost foam casting among many. Two early spin-off industrializations were Wah Chang (wrought zirconium alloys for military and commercial nuclear applications) and Oremet (both wrought and cast Ti). Both of these companies are now part of the ATI Allegheny Ludlum Corporation.

Introduction

In 1942 the forerunner to the Department of Energy's Albany Research Center, the Albany-Oregon-Station of the US Bureau of Mines, was founded with the purpose of "studying the application of electrical energy to the processing of minerals of that region." The abundance of electrical energy came from the Northwest's numerous hydroelectric dams. The Albany Research Center has a direct electrical feed from the Bonneville Lock and Dam on the Columbia River (which is operated by the US Army Corps of Engineers). Two minerals of interest which occurred in the Coos Bay region of the Oregon coast were chromite, $(Fe,Mg)Cr_2O_4$ and zircon, $ZrSiO_4$. Chromite is important since the United States needs a ready supply of chromium for heat resisting metals for aerospace and power plant applications. The importance of zirconium became apparent in the early days of the nuclear industry: zirconium is practically transparent to thermal neutrons and is thus the ideal container for nuclear fuel rods. In 1945 William J. Kroll joined the Albany-Oregon-Station as a consulting metallurgist. By this time, Dr. Kroll's process for making titanium was being explored for commercial use. By August of 1946, Dr. Kroll and his co-workers, Dr. B.A. Rogers, Dr. A. W. Schlechten, and Mr. L.E. Yerkes had succeeded in resolving the major metallurgical issues with zirconium and the first strip of Zr was melted and rolled [1]. The Albany-Oregon-Station melted and fabricated the zircaloys which ultimately became nuclear fuel rod cladding on atomic submarines: the United States Nuclear Navy was born. In 1956 Wah Chang (now part of the ATI Allegheny Ludlum Corporation) won the first commercial contract to produce zirconium for the nuclear navy.

Early Studies on Melting Zirconium

Zirconium, like its sister element titanium, can only be melted in high purity inert gas, or preferably in a vacuum. Vacuum arc melting is preferred as it is a convenient method for removing residual impurities such as chlorine and magnesium from the Kroll process. The early arc melting furnaces built at ARC were completely fabricated in-house (Figure 1). The furnace crucible was made of copper tubing with a bottom disk brazed into position with a copper-silver-phosphorous alloy. The top flange was similarly brazed on. The water jacket consisted of a coaxial stainless steel tubular shell. Initially, the vacuum housing above the crucible, the portion of the furnace that houses the electrode, was made of single wall stainless tubing with a cooling coil applied to the outside. These furnaces were powered by a bank of DC welders which could be energized in parallel. A toggle switch type control panel was used to add or remove welders from the circuit thereby adding or removing current to the melt. The electrode position was adjusted by the means of a reversible DC motor with a rack and pinion gear set. The quality of the arc and position of the electrode was determined by sighting down the bore of the furnace from either of two view ports. (Considering the high degree of potential danger viewing these melts directly, it is amazing that no critical accidents occurred.)

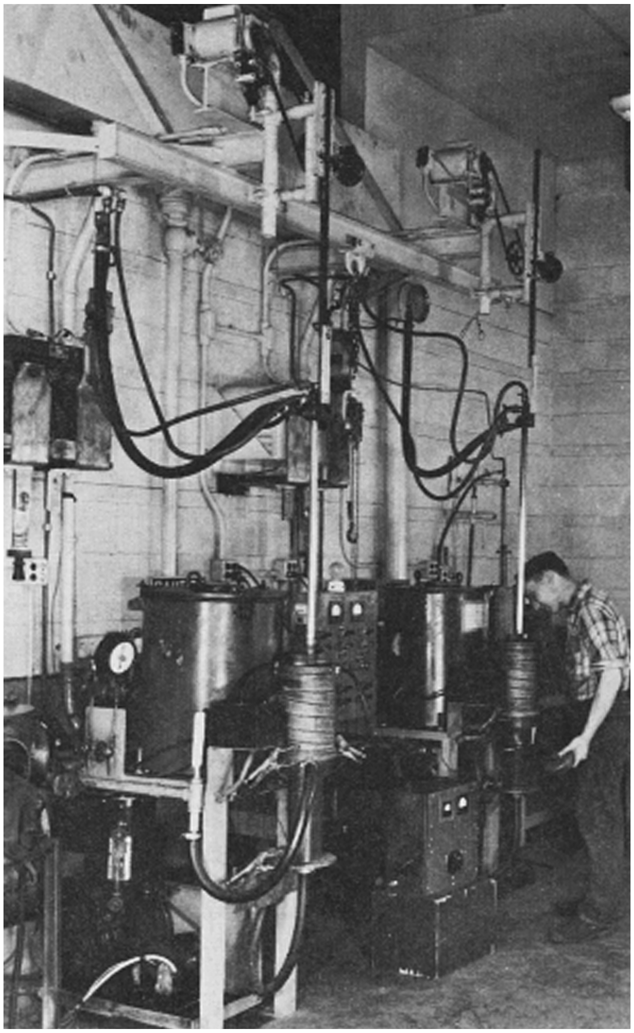

Figure 1: A pair of small consumable electrode VAR furnaces is shown in the photo above, from [2].

It turns out that two of the reactor grades of zirconium, zircaloy 2 and zircaloy 4, both contain about 1.4 weight percent Sn. This poses an additional difficulty due to the vast differences in melting temperature and density between these two elements (Zr: T_{mp}=1855C, ρ=6.5g/cc; Sn: T_{mp}=232C, ρ=7.3g/cc). In early experiments, the tin was simply pressed along with Zr sponge to form primary electrodes. However, it was found that the tin melted prematurely due to the temperature gradient that developed along the electrode during melting. As a result, the majority of the Sn was found in the bottom of the ingot. A device was conceived and built to chop and add Sn to the melt as a side feeder (Figure 2). While this device prevented the tin from melting prematurely, the higher density tin tended to sink to the bottom of the mushy zone of the ingot and resisted fully melting in (Figure 3). Stirring coils were added to the crucible body to aid in melting and distributing the tin, but it wasn't until these ingots were second melted that the tin distribution became acceptable [2].

Figure 2: An automatic tin chopper/feeder mechanism is shown in the photo above, from [2].

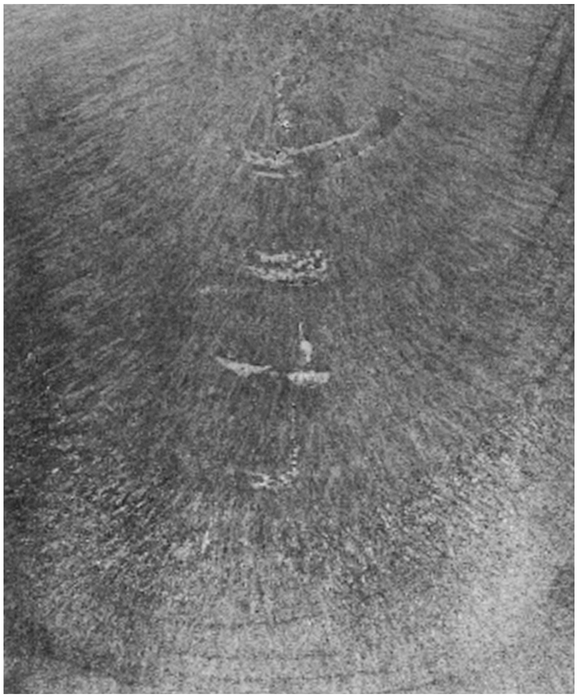

Figure 3: A zircaloy ingot cross section with undissolved tin (bright) is shown above, from [2].

Variables in Consumable Arc Melting

One of the earliest systematic experiments on arc melting that we are aware of occurred at the Albany-Oregon-Station of the US Bureau of Mines in the early 1950's [3]. This was a series of experiments conducted on a 2,250lb lot of zirconium. This material was first pressed into 2in x 2in x 20in compacts and melted into a 5in diameter crucible. These ingots were remelted into 8in diameter ingots which were subsequently quarter sawn, welded end-to-end and remelted. This remelt scheme comprised the core of a series of experiments. These experiments were conducted to better understand Melt Pool Depth, Melting Efficiency, Sidewall Studies (metal yield), and Arc Stability Studies. During these early days it appears that two of the main objectives of this study were increased melt rate and increased yield. This is understandable since it has a direct impact on the production of nuclear grade zirconium, which was the mission of the lab at that time and still has relevance today. We will briefly review their work here while the interested reader is directed to the original report [3]. The variables under investigation included current, voltage, vacuum levels, and current polarity (DC positive, DC negative, and AC).

Melt Pool Studies

Interestingly, this study was performed in order to understand the conditions under which the largest melt pool could be developed. The belief was that this promoted the best mixing of the alloy constituents (mainly Zr and Sn). Considering that zircaloys were the material melted most, this was reasonable since the partitioning rate of Sn and the other minor alloying additions between the solid and liquid is about equal. One of the important observations made during this work was that the ingot must be shrinking sufficiently from the crucible to greatly decrease the heat loss rate only slightly below the top of the ingot. These observations led to the discovery of very deep melt pools and ultimately the VAR casting trials (see the next section). The melt pool depths as a function of current and voltage for high vacuum conditions are shown schematically in Figure 4, from [3].

Melting Efficiency

First off, this phase of the study was not undertaken as an attempt to conserve electrical power. Rather the aim was to develop the deepest melt pool and thus provide for a more homogeneous ingot (this is certainly valid for zircaloys). Based on the assumption of a 75C superheat, the heat content of the molten metal was estimated to be 219cal/g. Converting this gives an electrical equivalent of 15.24 watt-min/g which equates to 65.6 g/kw-min which they used as their baseline estimate of 100% melting efficiency [3]. The results of their experiments are shown in Figure 5. It is interesting to note that the melting efficiency is very nearly independent of the input power. Rather, it is a strong function of vacuum level where a "good" vacuum was found to provide the highest melt efficiency. We feel that this is the earliest evidence that enhanced heat transfer between the ingot and the crucible wall can flatten out the melt pool, albeit, this is not what they were aiming to achieve. In modern production applications it is more common to provide a helium bleed on the ingot side to enhance this heat transfer in order to develop a flat melt pool [3].

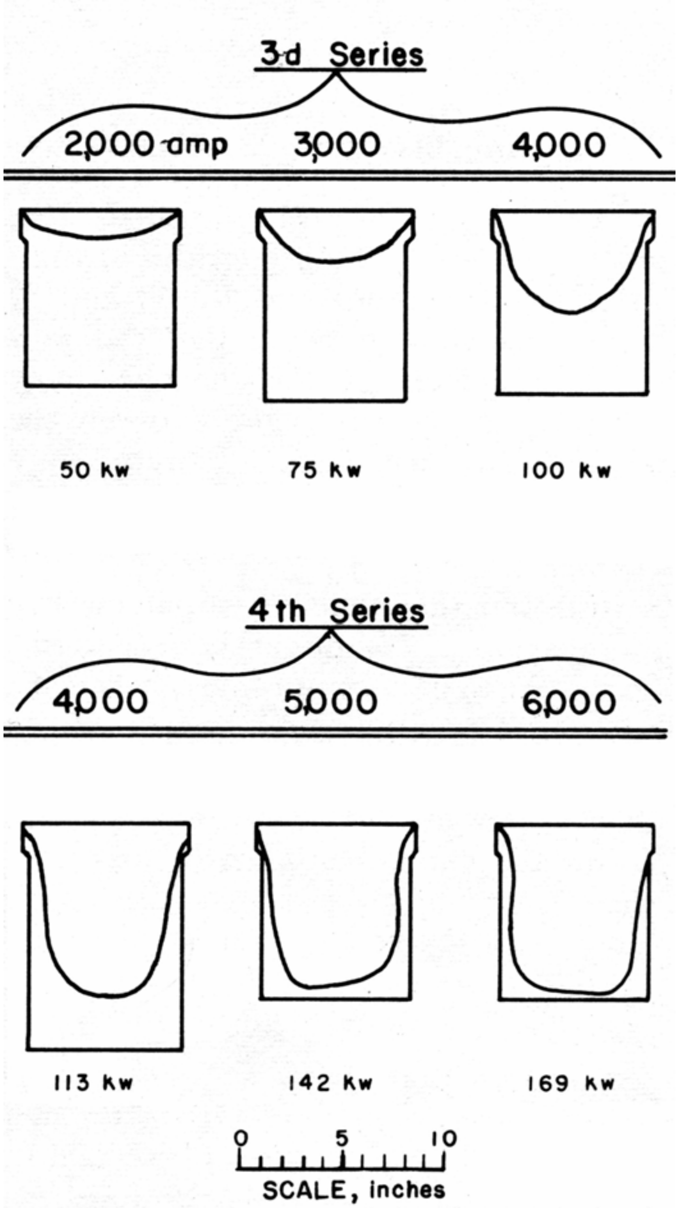

Figure 4: Schematic drawings of the melt pool shapes at the time when the power was cut are shown above (all these were run at straight polarity and high vacuum), from [3].

Sidewall Studies

As is well known in the industry, a good sidewall is desirable for high yields and is increasingly important as the ingot size

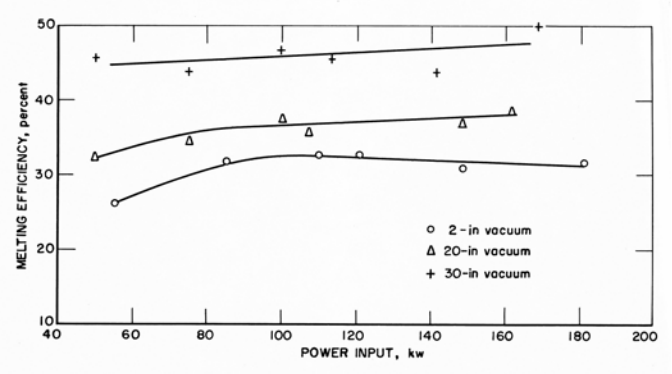

Figure 5: The results of the early melt efficiency studies are shown as a function of power input for different levels of vacuum (see text), from [3].

decreases due to surface-to-volume considerations. This much was understood even in the early days, and sidewall quality was of great concern to them. There was even a project which employed welding as a way to condition the ingot sidewall [4], although we are not aware of anyone employing that technique in industry today. The same experiments already described above were used to estimate the metal yield due to the quality of the sidewall. Ingots were sliced diametrically and etched. The largest sound diameter was measured and the square of this measurement was used to estimate the yield of a sound ingot. Since the ingots shrunk in a somewhat non-uniform manner from top to bottom, the crucible diameter was used to estimate the volume of a "perfect" ingot. Thus an ingot which was sound to its original cast surface would have a metal efficiency of about 97 percent. While the "metal efficiency" was found to be a stronger function of input power than the "melting efficiency", once again the vacuum level appeared to have a much stronger effect. The high vacuum melts had much higher metal yields (~82-90%) and also appeared to be a much weaker function of input power (Figure 6), from [3].

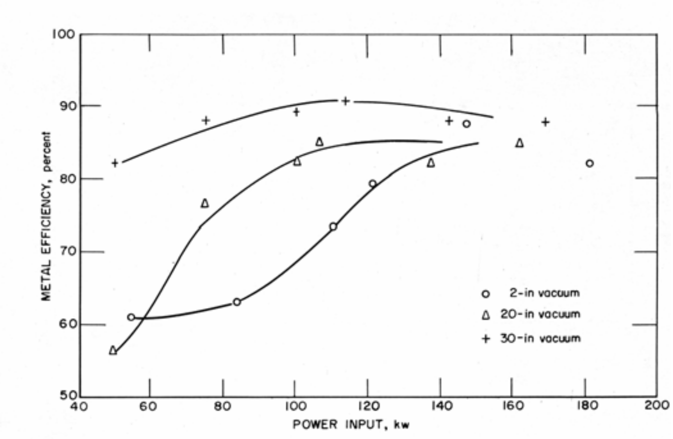

Figure 6: The results of the early metal (sidewall) efficiency studies are shown as a function of power input for different levels of vacuum (see text), from [3].

Arc Stability Studies

The discussion of arc stability in their study was rather limited. They did present an electrode voltage versus time plot from a chart recorder that was connected to a furnace and recorded the voltage as the furnace was evacuated from atmospheric to vacuum conditions. While the figure is not of good enough quality to reproduce here, it can be reported that the voltage fluctuated wildly at low vacuum and settled down nicely at high vacuum; thus a high vacuum was preferred. Further study of arc stability and high current metallic arcs was reported in a rather lengthy report by Wood and Beall in 1965 [5]. Not surprisingly, the main conclusion of this study [3] was that high power, straight polarity, and high vacuum melts were preferred. All of these settings produced a deep melt pool. These observations lead to the next study.

VAR casting of metals

In the early summer of 1953, the Albany Research Center was requested by the Department of the Army to explore the possibility of conducting research on casting titanium metal. The objective of the project was "to develop a technique for producing formed castings of titanium metal not less than 40 pounds in weight and without introduction of deleterious contamination." This was a very ambitious project since titanium is known as the "universal metal solvent" and also has a high affinity for common gasses. Additionally, the mechanical properties are adversely affected by small levels of contamination. Finally, consider the time-line: the commercial production of titanium had only begun in 1948, at DuPont de Nemours, with commercial ingots of titanium being produced by The Titanium Metals Corporation in 1950. In 1949 Kroll and Gilbert [6] had announced a method of casting titanium and zirconium shapes utilizing a graphite crucible heated by a graphite resistor. Additionally, Sutton, Gee, and DeLong [7] had demonstrated the use of induction heating using the same type of graphite crucible. Neither of these methods would produce titanium castings which would meet the present day carbon content standards.

In the early 1950's, several groups had developed a type of skull casting furnace which employed a non-consumable electrode [8-10]. These, along with the VAR melt experiments described above, led the Albany Research Center scientists to envision a consumable electrode VAR casting furnace. Ultimately, this work led to the award of a US Patent [11]. First, a series of experiments, similar to the zirconium work, was performed to establish the conditions under which a deep molten pool of titanium could be established. Not surprisingly, these were found to be similar to the conditions for deep pools of zirconium. Next in this development was determining a means to get the molten metal out of the crucible. A water cooled copper plug was employed. Using these basic techniques and a 14in diameter crucible, pour weights in excess of 100lbs were readily made (Figure 7). However, not all the pours were successful. Typical reasons for pours not being made were either that the copper plug was stuck or the skull proved too thick to melt through. At best, a success rate of ~75% (as a rate of heats poured) was obtained once the operational techniques were perfected. Additional difficulties included the general lack of control of when the heat was poured and this led to either under-filling or over-filling the mold, both of which were undesirable. Another complication was that frozen drips always formed around the plug hole preventing reinsertion of the plug. Drips continued to form even after the tap hole was enlarged to 6in. In this instance, they formed in the 2-3in diameter opening in the skull. While this latter problem did not impact the heat that formed the drips, it presented a logistical problem for follow up melts. As no acceptable solution was found, the development of an over-the-lip pour method was begun.

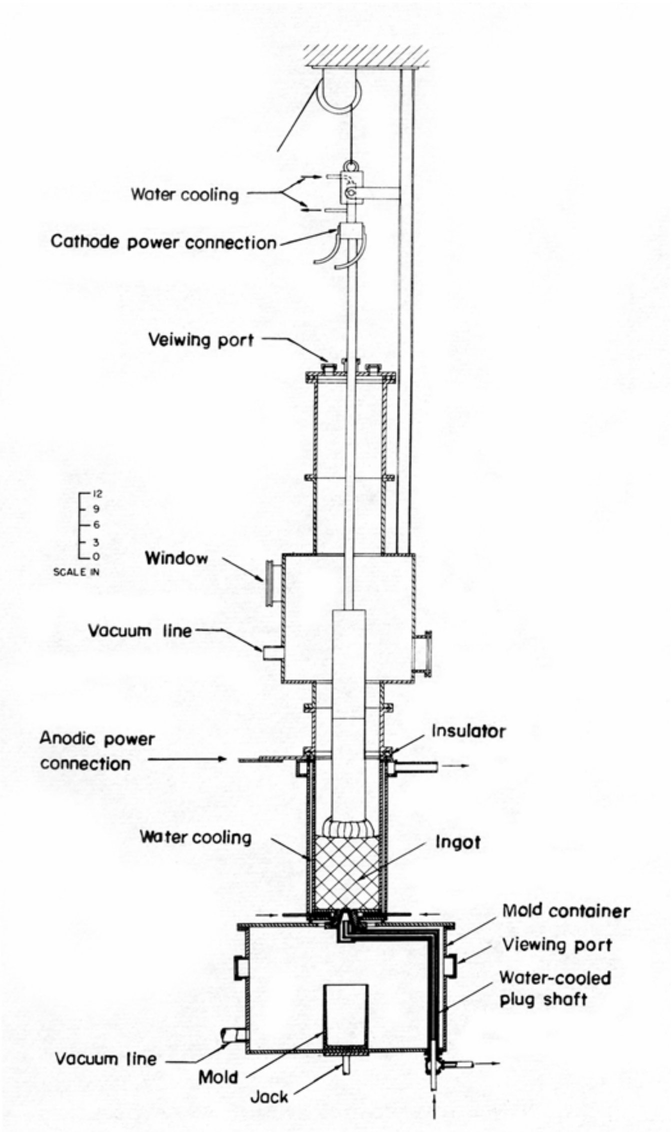

Figure 7: A schematic showing the basic design of a bottom pour VAR casting furnace in use at ARC in the early 1950's.

A schematic cut-away view of an over-the-lip VAR casting furnace is shown in Figure 8. Initially only one leg of the crucible was electrically active forming an "L"-shaped electrical path. This produced non-uniform melting of the electrode which was solved by energizing both legs of the crucible pivot. Much development was performed on the crucible shape with the final design being a slightly tapered round crucible with a low l/d ratio. Additionally, the lip of the inner portion of the crucible was rolled over and welded to the outer copper in order to keep the welded seam from experiencing liquid metal. The initial experiments on this small prototype furnace were very encouraging and the observations included: 1) the skull weight tended towards an equilibrium value, 2) multiple melts could be made using the same skull (in excess of 10 heats), 3) castings made with machined graphite molds had a die cast quality surface, 4) rapid cycle times were possible between heats.

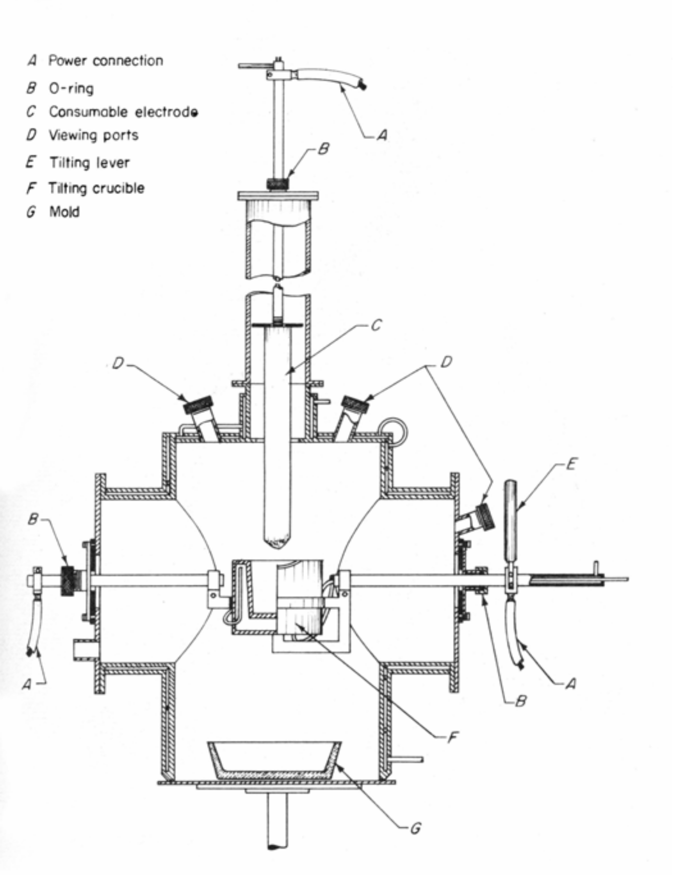

Figure 8: A schematic of one of the early designs for the improved, over the lip VAR casting design is shown above.

These initial successes spurred the construction of a larger furnace in 1955. This furnace was equipped with an auto-pour mechanism which retracted the electrode and poured the heat in less than 4 seconds once a limit switch setting had been reached. In this way, pour weights approaching 200lb were made. Coincidentally, Oremet was first incorporated late in 1955 with the construction of the plant beginning in early 1956 [12]. Eventually, Oremet went on to refine and melt titanium ingots. They also built and operated a large, over the lip VAR furnace similar to the larger version built at ARC.

Development of the Induction Skull Melter

One of the more innovative melting techniques that were developed at ARC was the induction skull melter developed by Clites [13, 14]. A quick search of the patent literature reveals that these two patents have been cited by 34 other awarded US Patents! The original crucible design included 4 water cooled copper crucible segments in the place of the more traditional ceramic crucible (Figure 9). Each segment was insulated from the next by an alumina rod and the melt charge included a CaF_2 slag (which was subsequently determined to be unnecessary). The development work continued on this furnace, and many crucible designs were tried over the years. A more refined crucible design is shown in Figure 10. This crucible uses a 32 tube-in-tube design to contain the melt. Modern versions of this crucible are only slightly refined.

Figure 9: Original design for the segmented, water cooled crucible.

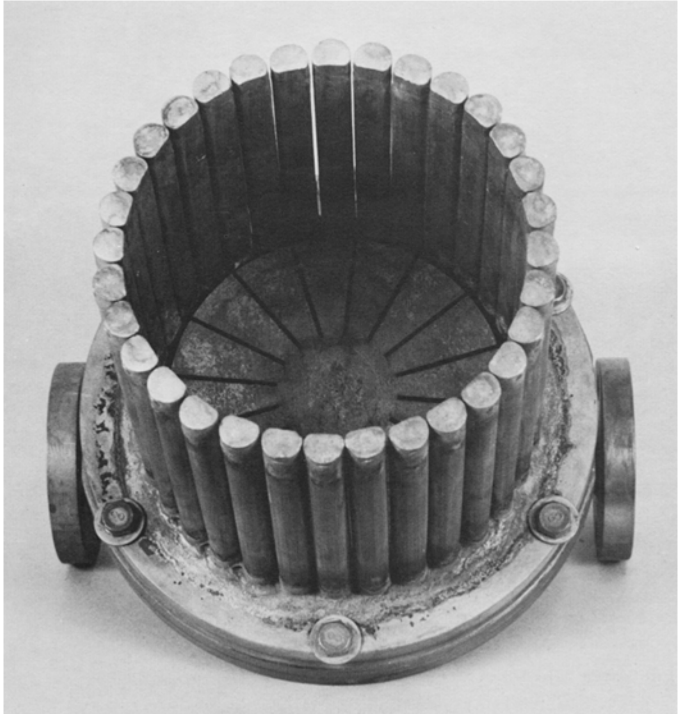

Figure 10: The more refined design for the segmented, water cooled crucible incorporating tube-in-tube cooling (5in diameter).

Clites et al. investigated both tilt pour and an ingot versions of his furnace design. The tilt pour version, along with the VAR casting furnace, were both workhorses in the investigation of mold materials for the reactive metals titanium and zirconium. One of the more successful materials from a technical standpoint was machined graphite. Figure 11 shows an intricate “laminated” graphite mold with a resulting titanium gate valve casting. The “lamination” facilitated the gentle relief of mold lock due to shrinkage of the casting [15]. Later on, a number of moldable materials were investigated [16]. Of these, the “rammed graphite” appears to be the only one to have been accepted commercially [17]. In a more recent implementation of the ingot furnace, Hartman et al. used this to supply a molten bath through which a metal rod (such as titanium) is drawn through to create a new, larger diameter rod [18].

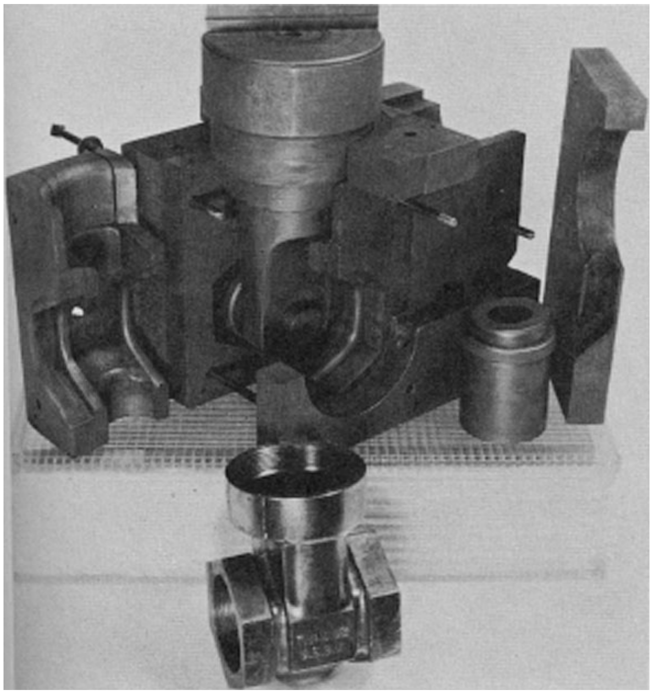

Figure 11: An intricate "laminated" graphite mold with a resulting titanium gate valve casting is shown above.

More Recent Liquid Metal Processing

We began this paper at the earliest days of what was to become the Albany Research Center (ARC). We briefly touched upon the work that was performed in the 1950's and 1960's, some of which led directly to the formation or strengthening of the local enterprises, Wah Chang (zirconium) and Oremet (titanium). We will now fast forward to briefly discuss some of the more recent melt processing research at ARC.

Cupola Work
The reader may be surprised to learn that research is being done on cupola furnaces, which is one of the oldest types of furnace known to man. Much of the work we performed on cupola furnaces was under CRADA agreements between the US Department of Energy and a private company. As such, that information is protected. Our 18in diameter cupola is fully instrumented to monitor temperatures, air flows, throughputs and off gasses and has been used for a number of experimental designs [19].

Gas Fired Furnace Work
An experimental pilot scale reverberatory furnace was recently built at ARC with the aim of better understanding the transfer of heat energy from the furnace flame to the walls and aluminum charge materials. This is important from an energy conservation standpoint since the overall industry-wide melting efficiency is about 25% [20]. Unlike so much of the early research at ARC that was conducted essentially before the advent of the computer age, we now try to incorporate computer modeling with pilot scale furnace operations in an iterative manner [21].

Electric Arc Furnaces
We have a very large range of electric arc furnaces at ARC which range from a 50lb, 50kW single phase furnace to a 2000lb 1MW, three-phase furnace with several variations in between. In recent years we have utilized these furnaces as thermodynamic vessels rather than simple melt vessels. For example, it was demonstrated that incinerator ash waste streams can be vitrified, and heavy metals thus better contained utilizing an electric arc furnace [22]. In another investigation, it was shown that spent primary aluminum pot liners can be processed in an electric arc furnace producing useful materials and destroying cyanogens and organics in the process [23].

Figure 12: A heat is shown above being tapped from our 2000lb three phase electric arc furnace.

Novel Casting Processes
The Albany Research Center's collaboration with the US Army has continued into the modern day. ARC cooperated with US Army Tank and Automotive Command (TACOM) to develop cast steel and titanium armor. An extensive development program was undertaken and ultimately, the conventional expendable pattern casting (EPC) process was successfully modified to produce these intricate castings. The most significant modifications included: 1) vacuum was applied to the sand molds, 2) continuous narrow-necked feeding systems were used to permit the casting of thin walls,

and 3) fixtures were designed to prevent pattern damage and to hold critical casting tolerances [24-25]. The cast armor plates (Figure 13) were 10 percent lighter than the rolled, forged, and machined production components. In addition, the ballistic results indicated that the cast armor was superior.

Figure 13: A P-900 hatch plate casting made using the expendable pattern casting process is shown above.

Alloy Development

We have a very active alloy development program at ARC [26-27]. The present focus is on developing metallic interconnect materials for use in solid oxide fuel cells. Also embedded into this work is the development of alloy materials with a controlled thermal expansion which also have applications in other oxidizing environments. Here too, we have incorporated computer modeling (e.g., ThermoCalc) and model verification into our research. It is interesting to note here that we used some of the same melting techniques such as VAR and induction melting along with machined graphite molds first developed by our ARC predecessors.

Acknowledgements

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References

1. H. Ketter, *William J. Kroll, A Luxembourg Scientist,* Imprimerie Fr. Faber, Mersch, Luxembourg (1998).
2. R.A. Beall, F. Caputo, and E.T. Hayes, *Homogeneous Alloys Produced by Consumable Electrode Arc Melting, Bureau of Mines Report of Investigation 5200 (1956).*
3. R.A. Beall, J.O. Borg, and F.W. Wood, *Study Of Consumable Electrode Arc Melting Bureau of Mines Report of Investigation 5144 (1955).*
4. F.W. Wood, J.O. Borg, and R. A. Beall, *Arc Ingot Conditioning by Sidewall Fusion, Bureau of Mines Report of Investigation 5149 (1955).*
5. F. W. Wood and R. A. Beall, *Studies of High-Current Metallic Arcs, Bureau of Mines Bulletin 625 (1965).*
6. W. J. Kroll, and H. L. Gilbert, *Melting and Casting Zirconium Metal, J. Electrochem. Soc.,* 96, 158-169 (1949).
7. J. B. Sutton, E. A. Gee, and W. B. DeLong, *Casting and Forging Titanium, Met. Prog. 58, 716-720 (1950).*
8. W. E. Kuhn, *Titanium and Zirconium Casting Now Practical, Mat. and Methods. 36, 94-95 (1952).*
9. R. M. Lang, *Shell Molds for Titanium Castings, Am.Foundryman, 25,60-62 (1954).*
10. O. W. Simmons, R. E. Edelman, and H McCurdy, *A Bottom Pour Arc type Furnace for Melting and Casting Titanium, Light Metals, 18,11-12 (1955).*
11. H. L. Gilbert, R. A. Beall, and J. O. Borg, U.S. Patent 2,825,641.
12. O. N. Thompson, *History of Oregon Metallurgical Corporation,* Oregon Metallurgical Corporation, Albany, Oregon, (1997).
13. P. G. Clites, and R. A. Beall, U.S. Patent 3,775,091.
14. P. G. Clites, U.S. Patent 4,058,668.
15. S. L. Ausmus, F.W. Wood, and R.A. Beall, *Casting techniques for Titanium, Zirconium, and Hafnium, Bureau of Mines Report of Investigation 5686 (1960).*
16. S. L. Ausmus,, and R.A. Beall, *Expendable Casting Molds for Reactive Metals,, Bureau of Mines Report of Investigation 6509 (1964)*
17. D. Kihlstadius, *Metals Handbook 9th Edition, Volume 15, Casting,* p 273, ASM International, Metals Park, Ohio (1988).
18. A. D. Hartman, E. R. Argetsinger, J. S. Hansen, J. I. Paige, P. E. King, P. C. Turner, U.S. Patent 6,342,102.
19. P. E. King, *Experimentation in Industrial Cupola, The Second International Cupola Conference,* American Foundrymen's Society, Inc., Des Plains, IL (1998).
20. T. Li, M. Hassan, K. Kuwana, K. Saito and P. E. King, *Performance of Secondary Aluminum Melting: Thermodynamic Analysis and Plant-Site Experiments, Submitted for publication in Energy, 2004.*
21. P. E. King, M. C. Hayes, T. Li, Q. Han, M. Hassan, and B. M Golchert *Design and Operation of an Experimental Reverberatory Aluminum Furnace,* Light Metal 2005.

22. L. L. Oden, and W. K. O'Conner, *ASME/US Bureau of Mines Investigative Program Report on Vitrification of Residue (Ash) from Municiple Waste Combustion Systems,* American Society of Mechanical Engineers, New York NY, 113 (1995).
23. W. K. O'Conner, P. C. Turner, G. W. Addison, U.S. Patent 6,498,282.
24. J. S. Hansen, P. C. Turner, *Casting P-900 Armorplate by the Expendable Pattern Casting Process, Bureau of Mines Report of Investigation 9436 (1992).*
25. P. C. Turner, R. R. Jordan, and J. S. Hansen, U.S. Patent 5,265,664.
26. J. S. Dunning, and D. E. Alman, U.S. Patent 6,475,310.
27. D. E. Alman, and P. D. Jablonski, *Low Coefficient of Thermal Expansion (CTE) Nickel Base Superalloys for Interconnect Applications in Intermediate Temperature Solid Oxide Fuel Cells (SOFC),* p 617 The Minerals, Metals & Materials Society, Superalloys 2004 (2004).