NIOBIUM ALLOYS AND HIGH TEMPERATURE APPLICATIONS

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Abstract

With the launch of the Soviet satellite Sputnik in 1957; a development program for scientific studies in the United States grew to fervor second only to the Manhattan Project. Niobium, then referred to as columbium, arose from a mere laboratory obscurity to a mature alloy family in less than 20 years. The quantity of material available grew from a few pounds to tons, while the applications literally ranged the universe. The development of other technologies, specifically those of electron beam melting and vacuum systems, were critical to the path of success for niobium materials. However, once the government funded programs subsided, the niobium alloys had to find niches where not only did their properties justify use but they could be economically justified as well. Niobium and its alloys are not rare and exclusive and are readily available for commercial applications. The gamut of alloys was at one time rich and varied but through economics rather than metallurgy this variety has been significantly reduced. Today, the primary application for high temperature niobium alloys is in one form or another of rocket propulsion. Despite considerable development work towards an oxidation resistant material, niobium alloys never successfully defeated their nemesis of catastrophic oxidation. Coating technology became a significant field of its own. Coating development paralleled the waxing and waning of niobium alloys. The scope of this work specifically omits a class of niobium-titanium alloys, many developed for “super-conducting” applications, some utilized in fastener stock, and a growing use for resistance to ignition in certain elevated temperature chemical processing environments.

Pre-Technology Chronology

Since the credit to English chemist, Charles Hatchett, in 1801 for the discovery of the element through the identification of a unique oxide in an ore sample, nearly 100 years passed before practical amounts of the metal and an application arrive. Except for the notation of a hydrogen reduction of a chloride in 1866 by Blomstand, the first quantities of the metal for evaluation did not appear until the beginning of the 20th century when Goldschmidt, Moisson and Von Bolton are credited with various reductions (aluminum and carbon reductions of oxides and sodium reduction of a fluocolumbate) (1). The considered application was the possible use as filament material in incandescent light bulbs (definitely a high temperature application for the time), circa 1905 and 1907(2). It would take approximately 90 years for a related application to manifest itself with Nb1Zr strip and tubing utilized in sodium vapor lamps. In 1929, Balke, using fusion electrolysis reduction and powder metallurgy, was able to produce rod and sheet metal for exhibition. We must wait a generation for the next major development in niobium (1).

In the 1930's niobium consumption grew through alloy additions to stainless steel and superalloys (2, 3). This use would grow significantly and ultimately have a positive impact on niobium development. The niobium (columbium until late 1970's) ore was at one point considered so crucial to the war (WWII) effort that it was reportedly flown into the country rather than risk loss at sea (4). For some time the extraction of niobium was dependent upon being a bi-product of tantalum refining. However, ultimately the process for obtaining high purity oxide from ferroniobium was developed and the discoveries of substantial ore deposits made for abundant supply (5). These combinations of circumstances were to eventually help niobium from being a restricted, exotic, and expensive material to an available, reasonably priced, engineering metal.

In the late 1950's, Wah Chang was producing niobium (as were other producers) by co-reducing the oxide and carbide to obtain a powder product, which was subsequently compacted, and resistance sintered. The resistance-heating step serving both a consolidation function as well as refining through the evolution of CO gas (6, 7). The material would then be wrought (forged or rolled) and re-sintered, reducing porosity and further refining the product. In the very late 1950's, aluminothermic reductions would be the standard procedure, but until the commercialization of electron-beam (EB) melting, all niobium and its alloys were generated through this process (followed by VAR melting). The small lot sizes (bars were approximately ? " X 1½" X 20-24"), combined with the reactions to form the carbide, the crushing operations, co-reduction, and thermal-mechanical processing (TMP) could not economically compete with the EB refining process (6).

The Real Beginning of Niobium and Niobium Alloy Metallurgy Came With The Commercialization of The Electron-Beam Melting Process

Contemporary with Von Bolton's reduction to metallic form to evaluate the properties of niobium at Siemens-Halske was Marcello Von Pirani's work, also at Siemens, and Halski's efforts in Berlin in 1905. This work lead to US patent 848,600, granted March 26, 1907 for use of electron beam for the melting of reactive and refractory metals (8). While some work continued with the use of the electron beam for evaporation of high refractory metals in the 1920's and 1930's, commercialization of the process would require further developments in technology (8). Electron beam melting requires a higher level of vacuum than the VAR (vacuum arc remelt, consumable electrode) process and a considerably higher pumping capacity. The mercury diffusion pumps were not up to the task, and it was not until 1937 that

L. Malter of RCA applied for a patent for multi-stage, self-fractionating oil diffusion pump. Large, multi-stage, oil diffusion pumps would not become readily available until developed for use on the Calutron electromagnetic isotope separation units of the Manhattan Project (9). The success of these pumps was in turn dependent upon the synthesis of low vapor pressure oils in 1928. NRC, eventually to become Varian, was formed in 1940, partially to provide vacuum pumps. VEECO (Vacuum Equipment Engineering Corporation) was founded in 1945 (9). Most of the diffusion pumps utilized on electron beam melting furnaces today come from these two sources.

Temescal (Stauffer-Temescal) was founded in 1953. By 1957 Temescal reports routinely melting three inch diameter niobium ingots (10). Quite possibly, some of this effort was toll work for Wah Chang. That year Wah Chang ordered the first commercial unit offered by Temescal, a 225KW unit, to be delivered in 1958. Second and third units were ordered in 1959 and 1960 (11). Ultimately Wah Chang would design and construct large furnaces of its own; those in operation today are internally designed and manufactured.

While niobium alloys are VAR melted for homogeneity, it is the electron beam refinement of pure niobium that makes them possible with low interstitial levels and absence of other trace elements.

The Great Impetus for Development

It is beneficial to understand some of the background of niobium alloy development and the atmosphere in which this development occurred.

In 1953 the Soviet Union exploded a hydrogen bomb, in 1954 the United States launched the atomic powered submarine Nautilus, and in October of 1957 the Soviets launched Sputnik. The "cold war" had begun. Grade school students were going through Civil Defense drills in case of nuclear attack. As the "Cold War" brewed, the nation's leaders, having recently experienced "The Great Depression", World War II, and the "Korean Conflict" were prompted by the launch of Sputnik to initiate a large effort of government funded research for dominance in defense and science. In the aftermath of the launch there was near hysteria in the United States about supposed inadequacies in scientific matters (12).

Several companies participated in refractory metal research. Most, if not all, of the following and others abroad were serious competitors in the niobium alloy arena: Wah Chang, Boeing, E. I. Du Pont de Nemours, Fansteel, Sylvania, Crucible Steel, Universal Cyclops, Shieldaloy, Union Carbide, Stauffer, Haynes Stellite, Kawecki, and General Electric. There are sparse references to British and Soviet niobium alloys as well. At the time, some of this development was classified and therefor not readily available. One of the more novel solutions developed in this era was Universal Cyclops "In-Fab" facility at Bridgeville, PA to eliminate oxidation of refractory metals during thermal-mechanical processing. The rolling mill, furnaces, and other equipment were enclosed in a sealed room, which was filled with argon; human operators entered in an abbreviated "spacesuit" through an airlock. I personally observed operations at one version of this configuration during a high school fieldtrip in the early 1960's.

In retrospect, it is easy to think that the product of that era was data and reports, especially in light of the few materials that remain in use today. This is the beginning of accelerated development, probably initiated with the Manhattan project, that we would see more of over the years. Also, this was the "age of discovery" for niobium, when any well presented and substantiated finding was a data point where none existed before.

An Early High Temperature Application – The Atomic Airplane

In this atmosphere of paranoia, perhaps typified by the McCarthy "Red Scares", combined with a gross misunderstanding of the capabilities of newly discovered atomic power, the atomic airplane project was conceived and nurtured. The concept of atomic powered flight originated as early as 1946 but began to take on the form of reality during the "atomo-mania" of the early 1950's. It was believed that automobiles and consumer appliances would be powered inexpensively by this new and mysterious energy source (13). No doubt, inter-service rivalry with the Nautilus development and purported rumors that the Soviets were developing a similar program fueled this misguided effort.

The initial concept (NEPA, Nuclear Energy for Propulsion, to become ANP, Aircraft Nuclear Propulsion) was a long range bomber that could stay aloft for weeks at a time (13). It was a concept that nearly died a natural death until the launch of Sputnik, when shortly afterwards was resurrected as CAMAL (Continuously Airborne Missile Launcher and low Level) (12). Contracts were awarded to Fairchild Engine and Aircraft, to GE for a direct cycle turbojet, and to PWA for an indirect cycle engine via a liquid metal heat exchanger. The PWA development was mostly at the component level at CANEL (Connecticut Aircraft Nuclear Engine Laboratory) (13). Two Convair B36H bombers were converted as testbed aircraft.

The concept was that as the turbojet engines initially took off under regular fuel, they would switch to superheated air flowing through the reactor on board and utilize this power source for the long term portion of the flight. Ultimately, GE successfully ran X-39, a modified J-47 jet engine under nuclear power with HTRE-3 (ground test) and the modified NB-36H flew several times with a live, operational reactor 1955 through 1957 (13, 14). There never was a nuclear powered flight. P&W did accomplish a great deal of design of liquid metal cooling loops, corrosion prevention, and heat exchanger design. However P&W work at CANEL never led to a test reactor (13). The logistics of shielding and weight involved clearly indicated that this was not a practical application for flight; however, the work with the liquid metal heat exchanger would directly translate to the space based reactor project. The ANP program ran until 1961, when it was cancelled by President Kennedy (14).

Additional work for NERVA (Nuclear Experiment for Rocket Vehicle Application) would continue the liquid metal/niobium environmental application. There is also a reference to NuERA (Nuclear Extended Range Aircraft) program as late as 1971.

The tubes for the liquid metal heat exchanger were supplied through Wah Chang (manufactured at Superior Tube) of Nb1Zr alloy for the first known high temperature application of a niobium alloy. To the best of our knowledge, the tubes were never actually integrated into a working design. The first tubes were pure niobium and then re-made as Nb-1Zr, being about ? " diameter (6). The Nb1Zr alloy, one of the earliest alloys studied, was being evaluated well before electron beam refined material was available and is still a viable alloy being produced today.

Birth of Practical Niobium Alloys

In 1959 through 1960, and later extended, Boeing Company and Wah Chang Corporation established a co-operative program to develop new and improved refractory metal sheet alloys. This was a systematic approach in exploring entire series of alloys believed to potentially yield materials usable for re-entry and other applications. The initial series was a "C" series of 23 niobium alloys, although there are report references to alloys up through C-256. The intent was

to melt buttons of these compositions and roll them to sheet product for evaluation (15, 16). Some compositions never made a successful button and others were never capable of being fabricated into sheet. This program was particularly well documented and while the end results of other companies were sometimes evaluated there is little available documented background on their development.

The alloy found to have the most promising combination of elevated temperature strength and fabrication characteristics was the C-103 alloy, which has a nominal composition of Nb-10%Hf-1%Ti (16). There is anecdotal reference to Steve Yih, then president of Wah Chang, encouraging researchers to find something Wah Chang could put lots of hafnium into; hafnium being separated through the extraction of nuclear zirconium and, at the time, becoming a burgeoning inventory. In 1961, the first production heat of C-103 alloy was produced by Wah Chang. The 500-lb heat was double arc melted from electron-beam-melted niobium, in keeping with the intent of the program to produce low interstitial sheet material. Alloy additions were made using commercially pure hafnium plate and commercially pure titanium rod.[16] The hafnium was known to contain approximately 3 percent zirconium as a remnant of the separation from zirconium extraction. This ingot was machined, canned, and warm extruded to sheet bar before being rolled into sheet (17).

The 1960's through the early 1970's were the heyday for niobium alloy development. Much of this development was strongly allied with the growing space program, a race for the moon (propaganda and national pride) and missile defense programs (the prevention of Armageddon) (18). A major concern was for re-entry shielding and hence high strength alloys at elevated temperatures. Early on, the catastrophic oxidation of niobium was a concern and along with coating development, there was the search for oxidation resistant alloys. Many of the high temperature alloys, solid solution strengthened primarily with tungsten and/or tantalum, proved resistant to traditional deformations modes and the oxidation resistant alloys lacked adequate physical mechanical properties (19, 20). There was also an effort, though somewhat smaller in scope, to evaluate niobium alloys for nuclear applications including liquid metal corrosion (space based reactor). The United Kingdom reportedly utilized some niobium material in a working reactor (21). Further investigation reveals that a niobium coupon was placed in the Dounreay Fast Reactor and while the use of niobium in lquid sodium loops is well known, no further elaboration was forthcoming (22).

There was an additional thrust in the later 1960's for developing alloys for turbojet engine applications and gas turbine applications. The program was for a high thrust, short duration engine, presumably a missile application (23). High strength niobium alloy, Cb 132M (duPont, Nb-20Ta-15W-5Mo-1.5Zr-0.2C), turbine blades were net-shape forged, and the plan was to encapsulate them within a yet-to-be-determined oxidation resistance niobium alloy (24, 25). Little optimism remained, though, in these endeavors for jet engine applications due to the lack of reliability of coatings in long cycle internal components and the inability to coordinate fabricability, creep strength, and room temperature ductility in turbine applications with oxidation resistance (26). The emphasis placed upon large sheet product resulted in the construction of larger EB furnaces for larger ingots and large, cold wall, refractory element and heat shield furnaces for annealing and coating. Through the 1960's, Universal Cyclops did considerable work on producing structural shapes ("Tee" and "hat" cross section beams) via rolling (under contract) in their In-Fab facility, largely from Cb752; however, I can find no reference to application of this material (27).

By the mid-1970's the surviving niobium alloys were largely the following:

- C103 Nb 10Hf 1Ti (Wah Chang/Boeing)
- FS85 Nb 10W 28Ta 1Zr (Fansteel)

• Cb129Y	Nb	10W	10Hf 0.2Y	(Wah Chang/Boeing)
• Cb752	Nb	10W	2.5Zr	(Union Carbide)
• Nb1Zr	Nb	1Zr		
• 30-09/15	Nb	30Hf	9W/15W	(Wah Chang)

The 3009 alloy is more a late comer than a survivor. It did not develop until the mid to latter 1970's and was perhaps the last great hope for an oxidation resistant niobium alloy in extended applications. The alloy was evaluated for high rate of fire gun barrels and rivet applications but no specific utilizations ever materialized.

Applications

Despite the extensive investigation of niobium alloys for re-entry applications, the main current uses of niobium alloys are essentially in rocket propulsion. With few exceptions, the niches for niobium alloys are the expansion chamber "skirts" for the larger boost engines, the combustion chambers and expansion "skirts" for orbit insertion or apogee control engines which are radiatively cooled, and the small vector or attitudinal control nozzles (28). The niobium alloy engines are typically bipropellent (monomethyl hydrazine and nitrogen tetroxide) fueled, hypergollic (ignited upon contact in combustion chamber), and are cycled several times in use (29). The large, boost, lift-off engines can be regeneratively cooled and they are so large that the cooling system inflicts no appreciable weight penalty; hence they can be constructed of steel or nickel alloys and even copper (28). Because of the secretive nature of early development, it is difficult to identify the first use of a niobium alloy component. The first refractory metal nozzle, made of Ta10W was built approximately 1958-59 and was believed to have flown circa 1960-61, naturally a classified program; the first niobium unit, again likely classified, can only be approximately placed as "the early 1960's" (30). However, Kaiser Marquardt documents their R-4D welded, niobium alloy and coated 490N (~110 pound thrust) engine as flying on Apollo 201, February 1966 (31). Another source does not give a date but believes the first alloy for this application was SCb291(Nb-10W-10Ta) (32).

Niobium alloys were considered for re-entry type applications for the Dyna-Soar X-20 program, an unpowered precursor to the space shuttle, which never matured very far beyond the drawing stage (a full scale mock-up was built).

A 1963 local (Albany, OR) press release mentions a large niobium alloy ring flange built for a rocket application, possibly attachment for Lunar Excursion Module (LEM) skirt (33). The most famous application, was perhaps, the skirt for the LEM which also served as a crash cushion upon descent, shows up in 1967 (26). C103 was used on the transstage nozzle extension of the Titan C-III. One of the largest structures fabricated from a niobium alloy (C-103) is the nozzle extension for the Apollo Spacecraft engine. The nozzle extension is a welded construction fabricated from the C-103 alloy sheet and tube and strengthened with ribs fabricated from C-129Y alloy. The nozzle extension for the LEM and the liquid rocket nozzle for the Lunar Hopper were also fabricated from niobium alloy C-103 (26).

One of the larger quantities of niobium alloy was for the post boost engine of the Minuteman missile deployed circa 1970 through 1978. This engine, generating approximately 20-25 pounds of thrust and designed by Bell Aerosystems, employed a SCb291 alloy (Nb-10W-10Ta, originating from Fansteel or Stauffer) for high creep strength and consumed a fluorine-hydrazine mixture requiring a tungsten and aluminide coating. For a period, several hundred engines a year were built from small bar stock. Later, another manufacturer, after extensive

investment in a C103 engine not selected, again submitted a C103 design now recognized for its lighter weight. The creep strength previously desired in SCb291 was apparently not considered necessary (30).

Currently, the Delta engine and the RL10 employed of the Shuttle are the last of the large engines with C103 skirts while Marquardt, TRW, ARC (formerly Royal Ordnance and now GD) continue to supply bipropellent (MMH/NTO) radiatively cooled apogee and vectoring type engines (veritable "Briggs & Strattons" of the satellite world) (29, 31, 34, 35). Iridium coated rhenium and refractory carbide matrix parts are challenging the use of C103 in these engines. Another related but slightly different application is the use of C103 in the valve bodies and related valve components in the gas management valves of the vectoring manifold for the re-entry vehicle of a currently deployed sea launched, intercontinental ballistic missile. That same re-entry vehicle manifold system also has a C103 reducer coupling (36). To date the only use of niobium alloys in jet engines has been the use of coated C103 sheet in the augmentor flaps comprising the afterburner of the F100 engine in the F15.

There is little optimism concerning the use of columbium alloys for long life turbojet engines because of coating reliability and the inaccessibility of internal components for frequent inspection of coating disintegration (26). There was a resurgence of niobium alloy development in the late 1960's and early 1970's for creep resistant materials with acceptable room temperature ductility for gas turbine applications. Solar Division of International Harvester and TRW (Thompson, Ramo, and Woodridge) participated in this work among others (37). Activity has essentially ceased in this direction. The F100 engine, despite revisions, is an older design and no niobium alloy has been incorporated into newer engines.

Coatings

For all practical purposes, there are no elevated temperature applications outside a controlled atmosphere for niobium alloys without the use of oxidation protection coatings. The catastrophic oxidation of niobium and its alloys was known among the earliest studies. While the 30-09 and 30-15 alloys were intended for such applications (Nb-30Hf-9W and Nb-30Hf-15W), they only gave a margin of safety if a coating was breached and did not offer "life of flight" oxidation resistance in the uncoated condition. Furthermore these materials had to be fabricated via powder metallurgy techniques and never saw commercial utilization even though made into rod and sheet. Other previous attempts at oxidation resistant niobium alloys never resulted in a material considered for actual fabrication.

Through 1960's and early 1970's, a variety of aluminides and silicides were applied as oxidation protective coatings. The aluminides were the earliest ventures and for lower temperature environments and/or shorter thermal cycles. As with the niobium alloys, the major coating development was also in that time period. There is still an interest in a coating with improved life and higher temperature resistance but not a demand for higher temperature niobium alloys. A multitude of compositions and processes where examined and evaluated, many of these quite complex and not commercially viable. A good coating requires a repeatable and controllable process, must coat all intended surfaces including faying or tightly jointed areas, interiors of small tubes and venturis, and must be NDT inspectable before "firing" and after the coating cycle is complete (38).

Depending upon the application, a satisfactory coating must successfully integrate many factors. These range from the extremes of temperatures encountered, the range of atmospheric and environmental situations that the engine will pass through (atmosphere, high space vacuum,

and combustion), the high temperature chemistry of combustion products, a variety of burn times and cycles including firing upon a space chilled component. Exotic fuel additives for enhanced performance can form disastrous eutectic reactions with the coating or base metal. There is the classic pesting oxidation phenomena at lower temperatures in atmospheric environments as well as gas erosion in a high velocity stream (39). To this must be added the requirements for ease of application and commercial viability. Exotic coating processes that can only be applied through direct line of sight and cannot reach deep, narrow aspect ratio interiors are unsatisfactory. Edges are particularly vulnerable to coating application error and subsequent damage.

The Hitemco R512E® (Si-20Fe-20Cr) coating originally developed by S. Priceman and L. Sama at Sylvania has become a well established commercial standard. There is a huge historical data base with R512E® applied to C103 (and other alloys) in a variety of environments and applications (30). There is also an R512A formulation in use. Any new coating has a significant market inertia to overcome and considerable qualification before consideration for flight hardware (32). However, it is in the area of coatings, that improved performance with C103 can be obtained toward the end of longer life and higher burn temperatures.

An Economic Culling

With the choice of ceramic heat shields for the space shuttle, the last hope for placement of a niobium alloy into a large-scale commercial application evaporated. The last Cb129Y was melted at Wah Chang in 1976 for Bill Black's evaluation for shuttle heat shields, the application lost out to "mummy dust" (40). There never was a commercially viable oxidation resistant niobium alloy. All the high strength, high temperature niobium alloys exhibited such difficulties in fabricating into normal mill products (sheet, bar, plate) let alone usable components that their use was significantly limited, if they were available in commercial quantities. The commercial uses, primarily in exhaust skirts and combustion chambers, in addition to a few other relatively small applications are all subject to the rules of a free economy and market place. It is axiomatic that with the demise of large scale government funding, private money and development effort equates to private, confidential data. The manufacture of niobium hardware is spread over a fractured group with each party concerned about protecting their technology and market share. In an increasingly competitive environment, focus has narrowed to the bottom line of components and materials at the expense of supporting technology.

Basically there ceased to be sufficient volume and economic justification for multiple or even alternate niobium alloys. C103 is left as the "one size fits all" material. The last FS85 was melted at Wah Chang in 1990. The heavy tantalum content has often worked against this material but it was a reliable, re-usable material. Reportedly Aerojet has some FS85 components on the Space Shuttle (30). Wah Chang had some nose caps deep drawn for an early 1990's NASP nosecone, heat pipe project from the last of the FS85. The last Cb752 was melted at Wah Chang in 1991.

While niobium alloys have, in some arenas, gotten the reputation as being rare, exotic and costly; in fact, C103 is readily available in most forms of mill products. Good quality niobium oxide, and hence niobium, can be manufactured from ferroniobium, which is consumed in hundreds of tons per year; C103 is not "unobtainium". Over the last three years Wah Chang shipments of C103 mill products has ranged from some 20,000 to 28,000 pounds. By nature of the processing, lead times are immutable and somewhat lengthy. The material does compete

with other materials for some applications and so remains to a large degree market priced; it is not inexpensive. If one considers a satellite package for launch that is effectively an investment of several hundred million dollars, the quantity of value-added C103 components is even a trivial amount of the orbit insertion/apogee engine package. Consider that for a hundred pound variety thruster, approximately 50-60 pounds of mill products are required in the form of bar and sheet to form the combustion chamber, expansion chamber skirt, and ancillary injector heads and those mill products might be in the $50/$100 a pound range. Subsequently the value added operations of forming, shaping, machining, welding, annealing, and coating increase that investment an order of magnitude. Depending upon the components being fabricated, some shaping techniques may provide advantages as, depending upon shop rates, it is nearly as costly to rough machine excess material away as it cost to put it there in the first place. The end result is that the "value-added" niobium components of the completed thruster package are perhaps less than 20% on the cost of that unit. The niobium alloy, even at the highest value-added form, is a trivial cost component of the satellite package, although crucial to it successful operation.

Unfulfilled Promise

Wah Chang constructed, under contract to a major aerospace company, a prototype niobium alloy nosecone that was a functional heat pipe. This work was for the NASP (National Aerospace Plane) project. This double-walled cone incorporated uniquely designed powder metal niobium capillary channels to deliver molten lithium to the point area of highest heat flux where it would evaporate. The lithium vapor would then conduct the heat away to the rearward, high surface area of the cone to radiate the heat away and condense. The unit was ultimately delivered to Wah Chang's customer and then to Wright-Patterson for evaluation. To our knowledge it remains untested, with the NASP project gone the way of the Dyna-Soar. Perhaps, if the concept of hypersonic flight becomes practical, niobium alloys and the heat pipe constructions will see actual use.

Recently Wah Chang constructed a combustion chamber of C103 intended for evaluation for use on a hypersonic missile, which would replace the current generation of cruise missiles. There was a press release on the successful test bed firing of this chamber and we are optimistic that C103 will serve well in this application. Time and funding will reveal the future of that project.

As early as 1973, Solar investigated tungsten reinforced niobium alloy composites (20). There is very little literature on niobium alloy composites, however, despite whatever strength advantages may have been obtained, the oxidation issue still remained. The objective was apparently to reinforce an oxidation resistant material that lacked high temperature strength with high strength tungsten wire. These materials could be horrendously expensive and only justifiable in rare cases.

Manufacture of Combustion Chamber

Most of the smaller units, 5 pound thrusters and smaller, are simply machined from bar stock. While, as mentioned earlier, the niobium alloy and its valued added processing are not significant portions of the entire propulsion unit, there are some cost savings worth looking at. The integral expansion chamber creates the demand for larger diameter bar stock. If sufficient quantities of units are being considered to offset tooling costs, the bar can be upset into a conical hollowed die and even back extruded with a conical punch. This process yields a

contoured envelope that effectively increases the material yield and decreases material costs somewhat (Fig. 1).

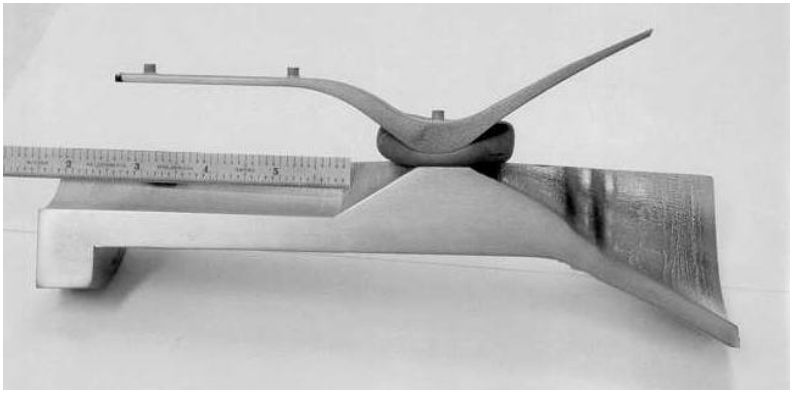


Figure 1: Forged Nozzle Section with slice from finished chamber.

C103 machines well providing one pays attention to its idiosyncrasies. The C103 chip does not break but comes off as a continuous strip; this can create havoc when machining tight inside contours such as the throat venturi in the smaller combustion chambers.

The size of Wah Chang C103 ingots is often based upon customer agreements and economics of required lot size rather than maximum power capacity. The grain size refinement possible in final bar or billet product is a consequence of the amount of TMP expressed in reduction of cross sectional area. Effectively, the grain size refinement possible in larger sizes of billet is limited. Additionally, a limited amount of TMP is required to achieve the physical properties desired. For the larger combustion chambers, "heading" the billet is often necessary to obtain the required flange diameter for the injector head and mounting of the engine. At the same time, there are benefits, aside from yield and machining savings, to be obtained by back extruding the conical exit section (Fig. 2). There is additional grain size reduction and a larger diameter mating section is possible for welding to the expansion chamber skirt making fit-up somewhat easier. A half cross section of a chamber, rejected for a mis-strike during forging, is shown for illustration. The reducer-coupling component for the manifold of a missile re-entry vehicle was produced by the back extrusion forging method. The tooling costs escalate with the size of the billet being forged and even more so with the addition of the split die for back extrusion; these costs may only make economic sense if a reasonable quantity of items is planned.

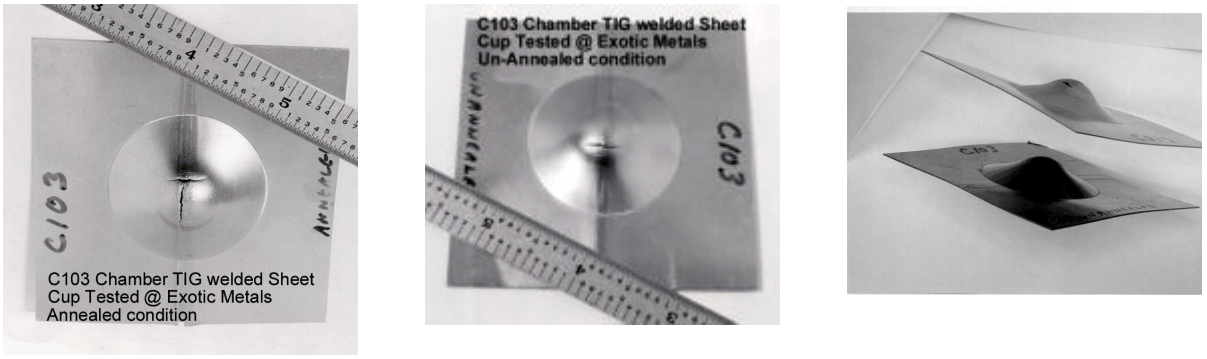
Figure 2: Forged C103 Bar to Nozzle Shape.

A stress relief anneal is recommended for any machining subsequent to forging for other than a clean-up, rough cut. While the cleanliness requirements for niobium alloys are always stringent, the closer one comes to final components, the more disastrous the results of violating those commandments. Contamination of furnace atmosphere, failure to pickle prior to annealing, or contamination with any eutectic former, copper, or material, which might break down at temperature and react with the alloy, may create undesirable phenomena. At this point, the chamber OD may be finish machined, although it is a consideration to leave additional envelope on the interior to permit locating the exact throat contour after the skirt portion is welded on.

Welding is usually performed as electron beam welding. Stringent weld preparation is necessary in terms of joint configuration and cleanliness prior to welding. Typically for a new configuration, it is wise to return to a bead-on-plate check for depth of penetration and then constructing a mock joint fit-up to be welded for evaluation prior to welding flight hardware. In addition to exercising rigorous cleanliness, discipline is required for the tacking and welding sequence to obtain good alignment of the chamber axis with the skirt axis.

Skirts, Mini and Maxi

The skirt or expansion chamber's purpose is to direct the exhaust gases to maximum effect and velocity for most possible thrust. The larger expansion chamber skirts are constructed of sheet metal welded, rolled into cone, and bulged (mechanically, hydrostatically) to contour. For carefully done, well-shielded welds, as in these chamber TIG welded specimens, there is a surprising amount of ductility. These were informal cup tests on nominal 0.030" sheet performed by Exotic Metals Forming to evaluate the capability of the material for hydrostatic bulge forming to net contour for prototype NASP heat pipe nosecone (Figures 3a, 3b, 3c). Generally, it is desirable to have as few of welds as possible to limit the exposure to failure and reduce manufacturing time. For the largest units, it may be advantageous to have the largest size sheet as possible but when balanced against the lead times and costs of outside conversion rolling, the demand has yet to materialize for someone willing to pay the cost and delivery penalty. For some units it may be practical to bulge two or three truncated conical sections and then weld them along the diameters. The final coating cycle is an effective stress relief.



(a) (b) (c)

Figure 3: Informal cup tests on nominal 0.030" sheet.

The smallest of skirts that are manufactured as separate from the combustion chamber may be deep drawn, spun, hydroformed or otherwise wrought into shape. For small items, few in number, the most economical route involves the fewest steps and so that material yield and machining costs are hardly a consideration. When multiple forming operations are required and

hence intermediate annealing, which require necessary pickling, and cleaning operations, the logistics of shipments and handling can become chaotic and potentially detrimental to the piece. Furthermore, in order to provide an adequate machining envelope for the part contour, the "preform" or blank was maintained at a substantial thickness, which subsequently has to be machined, often down to 0.010". In the early 1990's we questioned using the flow-turning or shear-spinning process to manufacture skirt preforms. Reportedly Royal Ordnance had employed a German firm to flow-turn some skirts to net shape and dimensions. The difficulty lay with the exotic reputation (if anyone had actually heard of the metal) of C103, the reluctance to devote precious production time to experimentation, and the investment by Wah Chang in development material.

Deep drawing and spinning involve sort of a wrapping of the blank around a mandrel in the shape of the part to be rendered. In these processes the blank size is on the order of a diameter of twice the part length. While some thinning may take place, neither process results in substantial reduction in thickness and can actually upset material in some cases. The flow turning, shear spinning or "chipless machining" process employs a blank the same diameter as the component and reduces the thickness substantially as the blank is worked over a spinning mandrel. Wah Chang was fortunate in developing an excellent working relationship with PMF Industries in Williamsport, PA. In 1992 PMF formed three straight-sided cones, 3.65" deep with minor and major diameters of 1.7" and 42" with a 5.1" diameter flange (Fig. 4 & 5). The 0.108" C103 stock was thinned uniformly to 0.047" in the cone area while the flange and small end remained the original thickness. Surface finish was excellent and the wrought structure recrystallized at 2200ºF. without growing grain in the unworked areas (Fig. 6 & 7).

Figure 4: Flowturned C103 Cone.

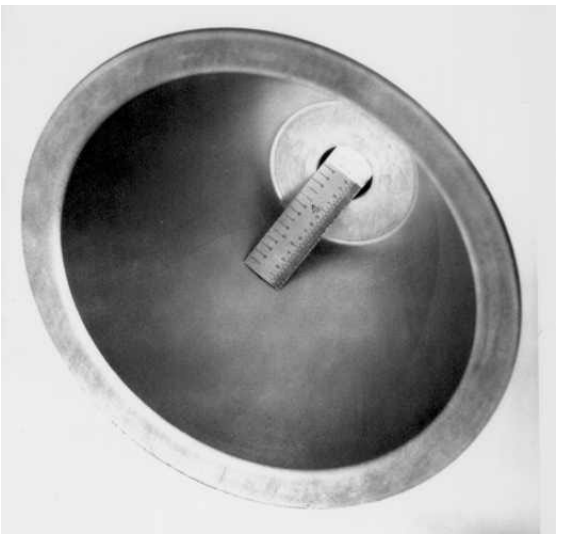


Figure 5: Interior Flowturned C103 Cone.

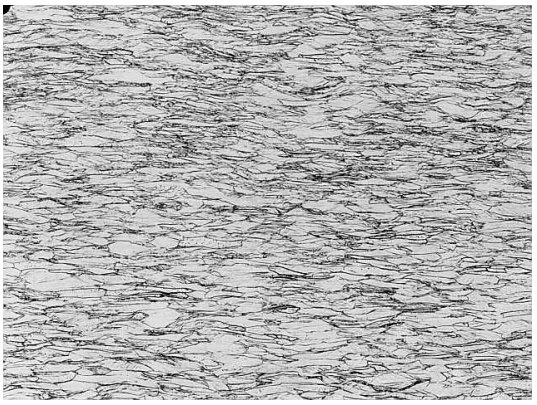


Figure 6: 100X Micro grain C103 Cone.

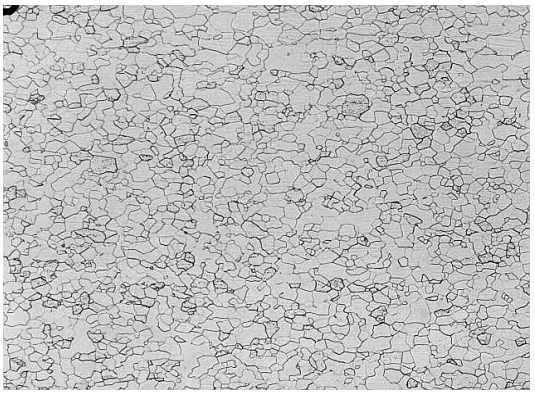


Figure 7: 100X Micro grain C103 Cone 2200ºF.

The next phase of the development of flow-turning C103 for an exhaust skirt was making actual parts in mid-1993 for a nominal 100# thrust unit. In order to maintain the required sine function of the angle of the preform, PFM developed a proprietary, bowl shaped, deep drawn, preform. The first components had problems with severe surface scuffing and galling (Figures 8, 9, 10). Ultimately this issue was resolved through, among other corrections, a unique two step lubrication process for the blank outside diameter. Ultimately successful components were obtained and incorporated into flight hardware. Wah Chang never pursued net-shape components as the volume of units was never sufficient to overcome the cost/benefit ratio. We always preferred a skirt blank with adequate machining envelope to permit fit-up with the combustion chamber with a good margin to permit machining the final part contour within the blank.

Figure 8: Flowturned C103 Exhaust Skirt Preform.

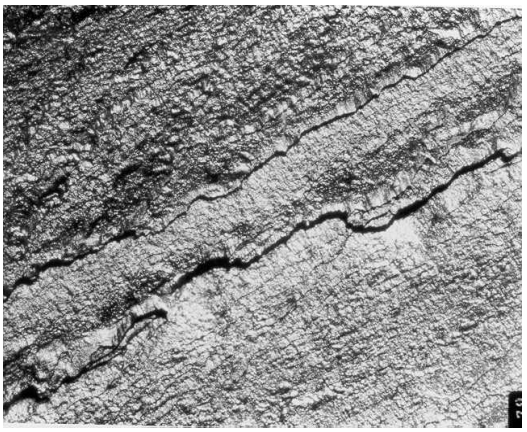


Figure 9: Surface Tears Preform ~ 13X.

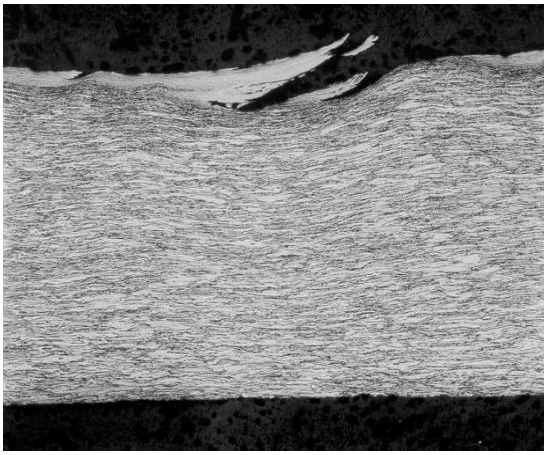


Figure 10: Section of Surface Tear ~ 45X.

The ultimate test of this product-process combination came in 1997 when Wah Chang began work on an 800 pound thrust engine, combustion chamber and skirt machined for flight use. Once some difficulties in manufacturing the pre-form shape were overcome, the meter long skirt blanks were formed in a single pass for each unit. These parts represented the current limit of size capacity for PFM Industries (Figures 11, 12).

Figure 11: Flowturned Large Exhaust Skirt Preform.

Figure 12: Skirt Preform welded to Combustion Chamber.

Conclusion

Niobium alloy(s) have demonstrated effective performance in certain niche applications. Pending other developments with competitive materials, these niches may remain secure or erode. Unless new programs for current types of applications develop or new applications arise, the current market for high temperature niobium alloys is limited. While other materials challenge niobium alloys, specifically C103 in the realm of rocket propulsion and satellite positioning, the cost to benefit analysis is not well established. Also, actual flight use of these challengers is limited. United States export regulations further limit applications for C103 and any of the other alloys (actually all satellite technology). Utilization of niobium alloys outside the United States and NATO domain is relatively unknown. There are whispers of foreign material being proffered, but whether or not the world market is attractive enough to sustain a competitor to C103 has yet to be determined.

As we currently employ niobium alloys, it would take a significant impetus to create a substantial increase in usage; something on the order of either a well funded, manned, international interplanetary expedition or a massive, singular threat to international peace and concomitant arms build-up. Hypersonic flight applications, either as leading edge material or for scramjet combustion units may present opportunities. The large, government funded programs (especially the multiple, parallel path efforts) that spurred niobium alloy development is unlikely to reoccur. The creation of a larger booster, with larger exhaust skirts, may boost consumption of C103 sheet somewhat. It appears unlikely that any of the past alloys may be resurrected unless some unique niche opens up. Free market dynamics prevail, and like other specialty materials niobium alloys will be established where their properties present a good value relative to their cost.

Improved coating performance could extend the range of niobium alloy use. A combination of economics and performance issues will drive niobium alloy high temperature applications in the future. Niobium alloys have demonstrated a proven track record of good performance and high reliability. While, perhaps lacking the interest and appeal of some of the newest composites, the technology is well established and commercially available.

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