HISTORY OF THE DEVELOPMENT OF ZIRCONIUM ALLOYS FOR USE IN NUCLEAR REACTORS. . . .

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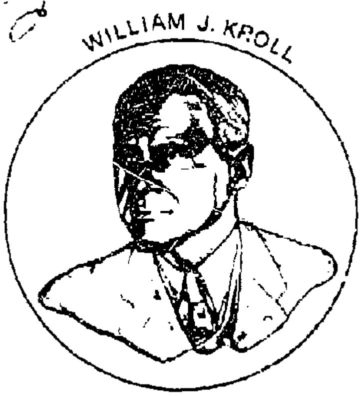

ON THE OCCASION OF THE
PRESENTATION OF THE
WILLIAM J. KROLL MEDAL
TO
ADMIRAL H.G. RICKOVER, USN

Denver, Colorado — March 21, 1975

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HISTORY OF THE DEVELOPMENT OF ZIRCONIUM ALLOYS FOR USE IN NUCLEAR REACTORS

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FOREWORD

Upon being notified of my selection to receive the William J. Kroll Medal for Zirconium, I thought it fitting to outline the technical problems and the major decisions made during the early development of zirconium alloys for use in naval reactors. It also seemed appropriate to compile a more detailed account of these events to supplement my remarks at the Medal presentation. Therefore, two of those most deeply involved with zirconium development for naval reactors were asked to prepare papers outlining the key events associated with this evolution.

The first was Mr. Lawton D. Geiger who was Manager of the Pittsburgh Naval Reactors Office of the Atomic Energy Commission from its establishment in 1948 until his retirement in 1973. He was directly involved in the early procurement of zirconium for all Commission needs including naval nuclear reactors. The second was Dr. Benjamin Lustman who, starting in 1949 was a metallurgist and currently is a manager responsible for core materials development at the Bettis Atomic Power Laboratory. He has been directly involved in the development of zirconium and its alloys as well as their application to naval reactors. Their papers, together with my speech presented at the Medal Award ceremony on March 21, 1975 in Denver, Colorado, are assembled in this report.

I have fostered the publication of the technology developed as part of the Naval Reactors Program. Eleven books have been published under the sponsorship of Naval Reactors. Three of the books deal with the materials covered in this report. They are:

> "Metallurgy of Zirconium," edited by B. Lustman and F. Kerze, Jr., July 1955, McGraw-Hill Book Company, New York

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"The Metallurgy of Hafnium," edited by D. E. Thomas and E. T. Hayes, 1960, available from Government Printing Office, Washington, D. C.

"Neutron Absorber Materials for Reactor Control," edited by W. Kermit Anderson and J. S. Theilacker, 1962, available from Government Printing Office, Washington, D. C.

My deep appreciation goes to Mr. Geiger and Dr. Lustman for their work in preparing their papers.

H. G. RICKOVER
ADMIRAL, USN

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THE DECISION TO USE ZIRCONIUM IN NUCLEAR REACTORS

by

Admiral H. G. Rickover, USN

William J. Kroll Medal
Presentation, Denver, Colorado
March 21, 1975

THE DECISION TO USE ZIRCONIUM IN NUCLEAR REACTORS

Admiral H. G. Rickover, USN

I am honored to be the first recipient of the William J. Kroll Medal for Zirconium. It is gratifying for me because it gives me an opportunity to pay tribute to an outstanding scientist.

I came to recognize his extraordinary qualities in the late 1940's and early 1950's. At that time nuclear propulsion for naval ships was far from a reality. Those of us working on the project faced problems at every hand. One of the most crucial was the development of a production process to obtain zirconium once the material was chosen for use in the nuclear reactor. We did not know whether the metal could be produced in sufficient quantities or to the rigid specifications needed for naval reactors.

Dr Kroll had worked on the development of a zirconium production process at the Bureau of Mines facility at Albany, Oregon. I made several hurried trips to see the work being done at that facility to furnish zirconium for the first naval reactors. Usually Dr Kroll, then a consultant to the Bureau of Mines, and several senior officials of the Bureau of Mines met me at the Portland airport on Friday evenings. We would drive to Albany, inspect the equipment, and discuss the results of the production effort then underway. Dr. Kroll always gave me straightforward answers. He was a scientist. I am an engineer. Our common interest was zirconium. I think we both understood the problems the other faced. I believe we had this understanding because we based our discussion on principles.

Dr Kroll was convinced that great advances in science came through the efforts of individuals. He himself exemplified

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this philosophy As he wrote in 1955, his early work on zirconium was conducted at his laboratory in Luxembourg where his only assistants were an unskilled laborer, a mechanic, and a secretary I also have found in my 57 years of naval service that engineering problems are most often solved through the efforts of technically competent individuals, not through the establishment of huge organizations or management systems.

Tonight I will talk about the decision to use zirconium and the principles that lay behind that decision. Circumstances change; events never repeat themselves exactly, but principles are long enduring. Much of what I shall say will be my personal recollections. I recognize, however, that without the zeal and hard work of scores of engineers and scientists from several organizations, zirconium would not be—as it is today—the major structural material in naval reactors and in nearly all of the reactors in central station power plants in the United States

THE ZIRCONIUM DECISION

In June 1946, I headed a few officers and civilians the Navy had sent to Oak Ridge. Our purpose was to see how nuclear energy could be used to propel naval ships. It was obvious that a nuclear powered submarine could revolutionize naval warfare. But a submarine nuclear propulsion plant posed severe requirements. It had to be compact so that it would fit into a submarine hull. It had to operate when the ship was rolling or pitching, or at an angle when it was diving or surfacing It had to be safe and reliable. It had to be rugged to meet military demands Finally, it would have to be operated by young sailors—men who were not scientists or engineers, but who would be carefully trained.

These are engineering problems At Oak Ridge, we were dazzled by the virtuosity of the scientists. They had accomplished much during the war. We soon discovered that scientists could give us only limited help. The goal of the scientist is to discover the laws of nature. The engineer uses and must obey those laws. The difference is fundamental. Theoretical concepts are crucial to science, but they can have a dangerous and hypnotic effect on individuals who are responsible for practical results. The engineer must seek out technical facts He cannot run away from them.

The decision to use zirconium in a nuclear reactor is an example of engineering judgment During 1946 and 1947, several groups of scientists and engineers were investigating metals for use in reactors Zirconium was one such metal. Stainless steel, aluminum, and beryllium were others The search was further complicated because several different types of reactors were under study One of the most promising of these approaches for naval propulsion was the pressurized water reactor However, for this application, a structural metal was needed which would withstand corrosion at high temperatures for long periods of time, which would maintain its integrity in an environment of intense radiation, and which would not absorb neutrons needed for the nuclear reaction Furthermore, if the Navy was to have a fleet of nuclear ships, the metal had to be one which could be produced in quantity and at reasonable cost Stainless steel, beryllium, and aluminum all had technical disadvantages which weighed against their use

Zirconium too, did not look promising Although its corrosion properties appeared reasonable, it was expensive and had never been produced in quantity In 1945, only a few hundred pounds were manufactured in the United States The cost was over $300 per pound Above all, tests showed that zirconium absorbed neutrons needed for the fission process

This situation changed suddenly While visiting Oak Ridge in December 1947, I learned that Dr Kaufman of MIT and Dr. Pomerance of Oak Ridge had just found that zirconium, as occurring in nature, was combined with the element hafnium. It was the hafnium at about 2 percent by weight which gave the zirconium the high level of neutron absorption. They were able to remove the hafnium in the laboratory and obtain zirconium which absorbed only a few neutrons. This was a scientific fact of great importance. At once I decided to choose zirconium for the naval reactor.

But the engineering problems were immense. At the time of this decision there was no assured source of zirconium, no estimate of how much would be needed, no certainty that any known or conceivable process could produce the required amount, and no specifications for the nuclear, mechanical, or corrosion qualities the metal had to possess. It was also possible that removing the hafnium could destroy the other qualities that had made zirconium worth investigating in the first place.

The decision was a logical choice for the pressurized water propulsion reactor. It was a risk, but all development is a risk. Once the decision was made we did everything we could to reduce the uncertainty. We did so by trying to find out what were the natural phenomena—which is only another way of saying that we were searching for technical facts. This is the responsibility of engineering—its challenge—and its ethical content. Several organizations helped us by running tests and performing analyses. This sounds simple, but it took us time to work out standards so that the efforts of one group could be compared with those of others. As research was going on to ascertain the engineering properties of zirconium, Dr. Kroll was continuing his work to improve the processes used to manufacture zirconium at low cost.

One reason for working on research and production processes simultaneously was to save time. We urgently needed zirconium for two reactors. The first was the Mark I, the land-based prototype to be built in Idaho to demonstrate the feasibility of installing a compact pressurized water reactor in a submarine. The second was the Mark II which would propel the *Nautilus*. But there was another reason. The reactor requirements for the chemical purity of the metal influenced the development of production processes; what we learned in one area had an impact on the other. We had to find out these relationships. As difficult as it was, in the long run it was better and less wasteful to carry on both efforts together. We were not thinking of only a few reactors, but of many nuclear ships.

One of the chief obstacles was administrative. I had no authority to obtain production quantities of zirconium. The Atomic Energy Commission and the Navy had established a joint organization in 1948 to develop nuclear power for naval ships. I was assigned to head this effort. In 1949, Westinghouse signed a contract and, after building a laboratory on the abandoned Bettis airfield, near Pittsburgh, began work on the pressurized water reactor. Soon we came up against a hard fact. The Bettis Laboratory needed zirconium. Procuring the metal was the responsibility of another organization of the Atomic Energy Commission. The indication was that the Commission, by following its procedures, could not procure zirconium on the schedule and in the quantity needed. I urged the Commission to authorize Bettis to manufacture zirconium for the Idaho reactor. The Commission overrode my recommendation.

I objected strenuously. I had been assigned the job of developing a nuclear submarine. The schedule called for having the ship ready for operation by January 1955—less than five years away. Zirconium at this moment was crucial in the development of the reactor. Further, this project was the only one committed to zirconium. The Commission was violating the principle that authority must match responsibility. I had been assigned the task, knew the facts, but other people were determining how my requirements should be met.

Certain factors were involved in the crisis. First, production application of the Kroll process was still under development and had not yet produced fully satisfactory metal. Therefore, we had to use the crystal-bar process which, at best, produced material of varying quality. In this technique bars were formed by deposition of a volatile zirconium compound on a heated filament. The individual bars were small and expensive. The Commission took the position that I should wait until a less costly process was available.

The Commission plan to procure the zirconium from a commercial company failed. As a result, Bettis in July 1950, was finally authorized to build a crystal-bar plant. Several organizations and facilities took part in supplying the zirconium needed for processing at Bettis. In August, the Commission transferred the authority to procure zirconium to my own organization. About 85 percent of the metal used for the Mark I reactor was made at Bettis. The rest came from industry sources. The successful operation of the Mark I, which achieved criticality on March 30, 1953, and reached full power on June 25, 1953, vindicated many technical decisions, among them the use of zirconium.

DEVELOPING IMPROVED ZIRCONIUM ALLOYS

There still remained the job of developing a zirconium alloy which would be cheaper to produce and would have less variability in corrosion resistance. In this process the Kroll technique would be the final production step and eliminate the need for the crystal-bar step, an important factor in reducing costs. Test programs at Bettis and elsewhere examined the effects of adding various elements to zirconium. Tin proved most beneficial. A committee composed of men from several organizations, who had actually worked on zirconium development recommended an alloy, later called Zircaloy-1, having 2.5 percent tin for the *Nautilus* reactor.

This was not a gamble. We had by now an active and experienced group of organizations capable of conducting tests and analyzing data. Even as preparations began to manufacture Zircaloy-1, we continued to test. By 1952, data showed that Zircaloy-1, in contrast to the usual behavior of metals, had an increasing rate of corrosion over time. It was clear that we could not use the alloy. Therefore, I stopped further processing of this alloy and began an urgent search for a new one.

Fortunately, Bettis already had underway an active program of corrosion tests. These included the study of a number of zirconium-base alloys which contained other elements to obtain improved corrosion resistance. Included was one ingot in which a small amount of stainless steel had been accidentally added. The tests showed the beneficial effects of iron, nickel and chromium, which are contained in stainless steel. This discovery was a good example of serendipity. But in another sense, it was not really chance. A well-run project should be able to recognize and take advantage of the unexpected.

Since the *Nautilus* was already under construction, I had to make a decision immediately. On August 28, 1952, I went to Bettis and reviewed the issue with scientists and metallurgists from Bettis and the Bureau of Mines. I approved their recommendation to establish an alloy which we subsequently called Zircaloy-2. I selected it for the *Nautilus* reactor before an ingot had ever been melted, fabricated, or tested for corrosion.

Again, the decision was a risk. However, it was made only after careful consideration of the recommendations of individuals who were actually involved in the work—not by managers or administrators. The basic composition of Zircaloy selected that day in August 1952, has continued, to the present, with only minor changes.

Bettis began manufacturing Zircaloy-2 for the *Nautilus* reactor. That reactor generated power on December 30, 1954, just one day prior to the date I had promised the Congressional Committee on Atomic Energy five years earlier. In less than a month, on January 17, 1955, the *Nautilus* got underway. This marked the beginning of the era of naval nuclear propulsion

Development of zirconium, however, still continued. The operational limit for Zircaloy-2 in a reactor was found to be dependent on its absorption of hydrogen during corrosion in high temperature water Bettis eventually found that replacing nickel with iron produced an alloy which had as good corrosion resistance as Zircaloy-2 but cut hydrogen absorption in half. This alloy, called Zircaloy-4, has since been adopted as the reference structural metal in most naval reactors produced after the mid-1960's as well as in most civilian power generating station reactors.

DEVELOPING PRODUCTION SOURCES

A basic reason for developing zirconium alloys was to lower the cost of production. This was important, for by the mid-1950's Congress had authorized several nuclear submarines. My staff and I estimated that our needs for zirconium would reach one million pounds a year within the next five years. Our policy was to procure the zirconium we needed from commercial sources. To do this we had to see that industry could get the information it needed to learn the specifications and the production process. We also had to convince industry that an attractive market existed

In April 1956, the Wah Chang Corporation contracted to provide 600,000 pounds of zirconium at a price just under $10 per pound. In a few months, under the direction of Mr Stephen Yih, they were in production Wah Chang has maintained its position of leadership. Over 70 percent of the zirconium made in the United States is produced at its facility in Albany

I also sought and received proposals from other companies. In that same year, contracts were placed with three other private organizations. These contracts were fixed quantity, long-term arrangements, aimed at providing the basis for companies to invest capital for large-scale production facilities. This action was the major step in achieving commercial production sources for zirconium. Over ten million pounds of zirconium and about a quarter of a million pounds of hafnium—which is also used in naval reactors—were delivered under these contracts between 1957 and 1963, at an average cost of about $6 per pound.

USE OF ZIRCONIUM IN ELECTRICAL GENERATING STATION REACTORS

The use of zirconium in reactors has not been limited to the Navy. It is also the major reactor structural material in nuclear central stations now being operated and constructed throughout the United States. The first such civilian power station was the Shippingport Atomic Power Station. In July 1953, because of my experience with pressurized water reactors, the Atomic Energy Commission assigned me the responsibility for this project. Under my direction the Bettis Atomic Power Laboratory designed, developed, and built this reactor.

Official groundbreaking took place on September 6, 1954. President Eisenhower, while visiting his wife's family here in Denver, used a neutron source to generate an electrical signal. This signal started an unmanned bulldozer at Shippingport to move the first earth on this project. The Shippingport reactor first began operation on December 2, 1957. This date was significant. It was exactly 15 years after Enrico Fermi achieved the first nuclear chain reaction at Stagg Field in Chicago. Within three weeks, the plant reached its full electrical power output which was distributed on the Duquesne Light Company transmission lines serving the Pittsburgh area.

Based on the operation of Shippingport and subsequent nuclear power plants, the commitment by electrical utility companies to nuclear power became much greater during the late 1960's and early 1970's. As of March 1, 1975, 55 nuclear powered electrical generating stations, with a capacity of over 39 million electrical kilowatts, were in operation in the United States. These 55 plants, operating at a 70 percent capacity factor, produce in a year the energy equivalent of 410 million barrels of oil, or 110 million tons of coal. All but three of these plants use Zircaloy cladding and structural material.

Based on the projected increased growth of electrical generating plants, it is estimated that by the mid-1980's the zirconium required for nuclear reactors will be about 15 million pounds per year. The metal will be supplied by a zirconium industry less than 20 years old, and using a process developed less than 25 years ago by Dr. Kroll.

CONCLUSION

I have emphasized in my remarks tonight that the decisions on zirconium were not gambles but risks. This does not mean that success was inevitable. It was not. What I have tried to show is that risk can be narrowed, but it is not easy to do so.

To say that it is necessary to obtain facts is little more useful than offering a soothing platitude. In engineering development, as well as in other fields, finding facts is arduous, exhausting, and time-consuming. They do not exist in isolation. The Romans looked at a constellation in the sky and called it Ursa Major. We call it the Big Dipper. The stars are the same, but we are different from the Romans. So it is with data: the use depends on your goal and your view.

The scientist can follow his quest in pursuit of knowledge; he can, to use popular figures of speech, explore an endless frontier or a boundless horizon. An engineer cannot. He has different responsibilities. He must proceed from one point to another. But even this is drastic oversimplification. The relations between means and the end are dynamic—a change at one point affects others.

It is this fluidity that places a particular responsibility upon the individual in charge of a development project. He cannot separate himself from technical work. He must not allow himself to be isolated by layers of administrators and managers. In Greek mythology, Antaeus was a giant who was strong as long as he had contact with the earth. When he was lifted from the earth he lost his strength. So it is with engineers. They must not be isolated from the real world.

When Dr. Kroll and I met at Albany, we dealt with details. We had to. We understood each other because we based our discussion on principles—his were scientific, mine were engineering. Far too frequently people, particularly those who have just come from universities, are convinced that if they learn the principles, that is all they need to know. As the decision on zirconium shows, this is not so. Of course you need principles, but that is not enough.

The Devil is in the details, but so is salvation.

DEVELOPMENT OF SOURCES OF SUPPLY FOR ZIRCONIUM AND HAFNIUM FOR NUCLEAR REACTORS

L. D. Geiger

DEVELOPMENT OF SOURCES OF SUPPLY FOR ZIRCONIUM AND HAFNIUM FOR NUCLEAR REACTORS

L. D. Geiger

This paper summarizes the development of commercial sources of supply for zirconium and hafnium metal over the period 1950 to 1965. The problems encountered in obtaining zirconium needed for early naval prototype and shipboard reactors are identified. Steps taken in the Government procurement process are described and statistics on production amounts, prices, and inventory are included.

The early problems led to centralization of all Commission procurement of zirconium at its Pittsburgh Area Office, later designated the Pittsburgh Naval Reactors Office. The actions leading to placement of five-year contracts with three companies in 1952 and 1956 which developed a commercial industry for zirconium are outlined. Throughout this paper I have referred to actions taken by Admiral Rickover, Director of the Atomic Energy Commission and Navy projects for nuclear propulsion of naval vessels and the first nuclear generating station at Shippingport, Pennsylvania. It is clear throughout the period covered that Admiral Rickover was the driving force in obtaining high quality zirconium at a low price from private industry through the use of market competition

PRELIMINARY PHASE

When Admiral Rickover first decided that zirconium would be the structural material for naval reactor cores, facilities for its production in significant quantities did not exist. In 1948 a typical price for the metal was about $235 per pound. In 1949 the Bettis Plant, later known as the Bettis Atomic Power Laboratory, was established by the Commission to pursue the nuclear submarine program. I was assigned as Manager of the Pittsburgh Area Office, which was set up to conduct the Commission's business at that Site.

Even though it was impossible at that time to determine with any certainty the amount of zirconium needed for the nuclear submarine project, there was little doubt that the figure would be substantial. Not only was metal required by Bettis for the Mark I prototype reactor being built for testing in Idaho and for the Mark II reactor being built for installation in the *Nautilus*, but also for several other Commission contractors and laboratories which needed purified zirconium for testing to determine the nuclear, mechanical, and corrosion properties of the metal.

With normal sources of supply unavailable, the procurement of zirconium was complicated and time-consuming. It was originally the responsibility of the AEC's Division of Production, which delegated it to the AEC's New York Operations Office. Under this arrangement, Commission laboratories and contractors needing zirconium submitted requests through their local Commission offices to the New York Operations Office, which sought suppliers for the combined requirements

The New York Operations Office had initiated contracts for zirconium metal development and procurement with the Foote Mineral Company of Exton, Pennsylvania, and the Titanium Alloy Manufacturing (TAM) Division of the National Lead Company of Niagara Falls, New York The New York Operations Office had also made an interagency working agreement with the Bureau of Mines to expand development and production capabilities for zirconium at its Albany, Oregon, facility. These arrangements constituted three alternate approaches to the production of zirconium metal Other Commission contractors were also involved Of these, the Battelle Memorial Institute of Columbus, Ohio, was a potential fourth source

Production of usable zirconium required the removal of an impurity, hafnium, which was associated with all zirconium ores. Technology to perform this purification was not available at that time outside of Commission facilities, but a suitable process had been successfully developed at the AEC's Y-12 Plant at Oak Ridge, Tennessee. During the preliminary phase of zirconium production, Oak Ridge was to supply purified zirconium compounds as feed material for metal producers.

TAM Division and the Bureau of Mines undertook to produce the zirconium as sponge metal formed from reduction of zirconium tetrachloride, while Foote Mineral Company and Battelle Memorial Institute were to produce crystal-bar zirconium—refined metal produced by deposition from a volatile zirconium compound on a heated filament.

Some of the other organizations that were studying zirconium properties and production methods at that time were the AEC's Argonne National Laboratory, General Electric Company as operator of the AEC's Knolls Atomic Power Laboratory, Massachusetts Institute of Technology, the AEC's Ames Laboratory at Iowa State University, National Research Corporation, Sylvania Electric Products Company, and the Bloomfield plant of Westinghouse Electric Corporation.

The research was often frustrating, partly from technical difficulties, partly from the shortage of materials to work with, and partly from the fact that no one was coordinating the several organizations involved. In addition, the tendency of some forms of zirconium to explode or burn rapidly represented a hazard

Admiral Rickover could not at first convince those responsible in the Commission of the urgency of the need for zirconium. They argued that because he could not set precise amounts needed or provide detailed specifications, a large production program seemed premature or unnecessary. Furthermore, they said that the work already in progress might resolve the uncertainties and lead to better and less expensive production methods than crystal bar, the only process which appeared able to provide suitable material.

IDENTIFICATION OF FIRST FIRM REQUIREMENTS

In early 1950 Bettis calculated a firm requirement for 30,000 pounds of low-hafnium, corrosion-resistant zirconium for the Mark I prototype reactor. Certain he would never get that amount of acceptable material to meet the Mark I timetable under the existing Commission procedures, Admiral Rickover encouraged Bettis in March 1950 to write an official letter to the Commission pointing out that, on the basis of past experience, there was little likelihood of obtaining enough zirconium to meet the required schedule. Therefore, the Bettis Laboratory requested Commission authorization to procure its zirconium directly.

The Commission, however, in April 1950 contracted through the New York Operations Office with Foote Mineral Company to deliver 30,000 pounds of crystal bar by June 30, 1951. The price varied from $110 per pound for the first 9000 pounds, to $50 per pound for the last 17,000 pounds, exclusive of the cost of the zirconium tetrachloride feed material. The basic plan of the New York Operations Office for meeting the Mark I and other requirements was as follows:

1. TAM Division would supply impure zirconium tetrachloride made from zircon sand which had been chlorinated by the Stauffer Chemical Company. The zircon came from the Rutile Mining Company.

2. Oak Ridge would perform the zirconium-hafnium separation. The Oak Ridge product would be low-hafnium zirconium oxide. Oak Ridge would convert some of the

oxide to tetrachloride, but also ship some oxide to the Bureau of Mines Albany, Oregon, plant and to TAM Division for further processing.

3. The Bureau of Mines would chlorinate some of the Oak Ridge zirconium oxide and would reduce the resulting tetrachloride and other tetrachloride from Oak Ridge to sponge. Also, the Bureau would convert sponge to ingot or strip, as needed.

4. TAM Division would perform much the same procedure as the Bureau of Mines. They would chlorinate some Oak Ridge-produced zirconium oxide and reduce the resulting tetrachloride as well as other tetrachloride to sponge. Processing of the zirconium strip for an Argonne reactor physics experiment was subcontracted to the Electro Metallurgical Corporation for melting and to the Simonds Saw and Steel Company for forging and rolling.

5. Foote Mineral Company would convert low-hafnium tetrachloride to sponge and then to crystal bar for delivery to Bettis and other users.

The plan failed. Foote Mineral Company sponge production was variable and produced low yields and poor grade material. The TAM Division also had high process losses and produced sponge containing impurities. Further, production schedules established by Foote and other producers did not meet requirements. As of July 31, 1950 about 4900 of the 6500 pounds of zirconium strip needed for the Argonne critical experiment had yet to be delivered. Bettis had received none of the 30,000 pounds of crystal bar needed for the Mark I reactor.

ASSIGNMENT OF PROCUREMENT RESPONSIBILITY TO PITTSBURGH

In July 1950, at Admiral Rickover's prodding, the Commission finally authorized Bettis to install and operate crystal-bar facilities of its own design and to use Government-furnished sponge as the feed material. Bettis crystal bar was to supplement or, if necessary, replace Foote Mineral Company production. The newly designed plant was based on the same basic process, but scaled up to produce larger crystal-bar stock.

In August 1950 the Commission transferred the responsibility for zirconium procurement from the Director of Production to the Director of Reactor Development, who assigned the responsibility to the Chicago Operations Office and through it to its Pittsburgh Area Office. Up to this point Admiral Rickover's group, called Naval Reactors, although responsible to the Commission and the Navy for developing naval nuclear reactors, had not possessed the authority to procure the metal essential for its work

After consultation with Admiral Rickover and Bettis, the Pittsburgh Area Office took several actions to modify the production plan. Since the Foote Mineral Company's sponge was friable and hard to process, that part of their operation was cancelled Because TAM Division sponge had excessive impurities and the production process was inefficient, this work was stopped. All hafnium separation was still done at Oak Ridge, and all sponge came from the Bureau of Mines and served as the feed material for Foote and for Bettis when its facility began operation in November 1950. This facility, which operated until June 1952, produced approximately 80,000 pounds of crystal-bar zirconium. About half of this amount was used in the manufacture of the Mark I reactor.

ZIRCONIUM FOR THE MARK I REACTOR

Several themes ran simultaneously throughout the early zirconium procurement program for the Mark I prototype reactor. First was the immediate objective of procurement of reactor-grade zirconium; second, the improvement of production processes; third, the development of zirconium alloys with improved qualities; and fourth, the creation of a zirconium industry. Although these items are considered separately, they were actually concurrent, and developments in one usually had an impact on the others.

Specifications for zirconium material for the Mark I reactor consisted primarily of general requirements for ductility, corrosion resistance, and absorption cross section for thermal neutrons Because the limits of physical properties and impurities could not yet be established, production was directed toward zirconium of the highest possible purity. Metal shapes produced from melting Bureau of Mines sponge, while meeting the ductility requirements, did not consistently meet corrosion resistance standards. Consequently, Admiral Rickover decided that crystal bar, the refined form of zirconium, would be used for the Mark I reactor.

The Bureau of Mines required additional capacity to produce the zirconium sponge needed at Bettis and at Foote to produce the required crystal-bar zirconium. The Bureau's pilot plant had been established with the encouragement and assistance both of the Navy's Bureau of Ships and the AEC's Division of Production With the reassignment of responsibilities in August 1950, the Pittsburgh Area Office financed the expansion in 1951. To cover expansion and production costs, the Commission used inventory funds which had been provided to pay for the zirconium ordered by various users. Most of the money came from Mark I prototype funds, but other zirconium users also contributed.

The Bureau of Mines soon became heavily involved in hafnium separation. Initial use of the Y-12 plant at Oak Ridge for this purpose was seen from the beginning as an expedient, but one which would distract the facility from its primary mission. Therefore the decision was made to have the Bureau of Mines Albany facility expanded to perform this operation. The Bureau began construction of additional facilities in April 1951 and started operation in April 1952. About a year later Oak Ridge was able to withdraw from all zirconium-hafnium separation work.

EARLY STEPS TOWARD INDUSTRIAL PARTICIPATION

Given the incomplete stage of technological development, the very tight schedule, and the uncertainty as to specification requirements, there existed no practical alternative but to use Government facilities to produce the zirconium needed for the Mark I reactor. However, as a basic policy, Admiral Rickover and the other Commission officials involved considered it undesirable for the Government to continue to produce zirconium. Therefore, actions were undertaken to develop one or more commercial sources of supply. Having witnessed the operations of both the Government and private industry during his Navy career, Admiral Rickover was convinced of the correctness of this basic policy

The initiative for stimulating zirconium industrial interest had to come from Washington. In March 1951 the Commission issued a press release announcing the intent to obtain zirconium and hafnium from commercial sources and asking for expressions of interest. On June 22, 1951 the Pittsburgh Area Office issued a prospectus to 26 companies which appeared to be the most likely candidates. The prospectus stated that the Commission proposed to ask for amounts of up to 150,000 pounds of zirconium annually for a period of five years, beginning in January

1953. The prospectus also included preliminary technical specifications and invited the companies to visit Commission and Bureau of Mines facilities for firsthand information.

The early contracts had contained no technical specifications because meaningful specifications had not been developed prior to this time; the scientists concerned merely stated that they desired the composition to be "as pure as possible." They also stated that the minimum strength limits were to be "as strong as possible without increasing hardness."

However, it was recognized that specifications were important in order to achieve normal procurement on a fixed-price basis. Therefore, specifications were drafted by the Pittsburgh Area Office and were commented on by Bettis, Naval Reactors, Chicago Operations Office, Bureau of Mines, and Argonne. The final Naval Reactors' approved version then went into the prospectus package.

With the prospectus, an invitation was issued to interested parties to attend a meeting on July 18, 1951, at the AEC's Chicago Office for a more detailed discussion. Thirty-four companies sent representatives to the meeting. These representatives vehemently disagreed with the plan to use a fixed-price contract, arguing that the future needs for zirconium and hafnium were too indefinite and the technical uncertainties were too great. Further, they argued that the annual delivery rates proposed in the prospectus were not high enough to justify building a production plant. It was difficult at the time, however, to justify as much as 150,000 pounds of zirconium a year on a continuing basis. Although it was expected that replacement cores for the *Nautilus* would be needed, and the study of a nuclear powered aircraft carrier had begun, other naval reactor projects were still nebulous. At this time the Mark I reactor had not yet begun operation so there was no certainty that the Navy would even adopt nuclear propulsion. Although there was talk of other uses of zirconium, there was no reasonably firm requirement by other Commission reactor development projects, nor by the Commission-owned plutonium production reactors

No contracts resulted directly from this meeting but it was nevertheless useful as a step toward the contract that was ultimately negotiated For one thing, it was a follow-up of the prospectus and made certain that those organizations interested in producing zirconium had access to the same information Also, the discussion enabled Commission representatives to better understand and answer questions which were troubling industry All of the companies were interested in obtaining a Government contract, but none was willing to accept the risk of building a new plant and committing itself to a fixed-price contract The meeting also revealed that within the Commission the Naval Reactors Program was the sole customer, notwithstanding vocal interest expressed by other programs By his insistence on industry-owned plants and fixed-price contracts, Admiral Rickover displayed his determination to keep the Government out of the contractor's business

To overcome some of the problems identified by the Chicago meeting, the Commission in September 1951 authorized acceptance of satisfactory bids for zirconium sponge in quantities not to exceed 300,000 pounds per year for five years An issue then arose about how to divide this amount of material among the bidders One position was to award the entire amount to a single company because such an action would result in the lowest price But a single source procurement could open the way to a monopoly situation Admiral Rickover desired two or more suppliers, he never felt comfortable with only one contractor for any purpose He also believed that long-range competition and greater reliability at lower cost would result from having two or more sources of supply

Leaving this issue unsettled, an invitation was issued on November 5, 1951, to more than 35 firms. The invitation requested fixed-price proposals to supply zirconium and hafnium sponge for five years, at annual rates ranging from 100,000 to 450,000 pounds of zirconium. The invitation was based on the terms and conditions of the standard Government supply contract, and offered no relief to the contractor for the risks involved. Among the standard contract provisions, the Government was to be able to cancel any contract for its convenience, and the contractor would have no way to recover the cost of his facilities.

On January 15, 1952 the bids were opened at Pittsburgh with six companies in attendance. However, none of the bids was responsive. The National Lead Company and the Air Reduction Company each submitted alternative proposals which were no more than offers to negotiate on substantially different terms and conditions than had been requested. Foote Mineral Company, Brush Beryllium Company, Faesy and Besthoff Company, and Nicholcarb Minerals Company (an affiliate of the Carborundum Company), while interested in obtaining a contract, declared that the terms failed to take account of their risk considering the uncertain future market for zirconium and hafnium. This result had been expected; it provided a legal basis under procurement regulations to proceed to negotiate a contract or contracts.

Within a week a Zirconium Contractor Selection Board was established. The job of the Board was to recommend one or more contractors to produce 300,000 pounds of zirconium and related hafnium per year for a period of five years. On March 22, 1952, after meetings with the most likely suppliers, the Board recommended dividing the amount equally between the Carborundum Company and the Foote Mineral Company. Both had proposed in writing to build their own plants subject to certain conditions. For a limited time the Commission would reimburse actual start-up costs, but with no profit for the companies. After this period, the Commission would pay a unit price for metal which met specifications. To resolve the problem of the Government's right to cancel, the proposals specified Government payment for the unamortized facility costs if the contract was terminated before the five years were up The unit price was to be redetermined each year to cover labor escalation and to share any other changes in actual production costs between the Commission and the contractor

Of the two proposals, that of Carborundum included the lowest price for zirconium and contained the fewest number of legal conditions Negotiations with this company proved successful and a contract was signed on May 13, 1952, with the Carborundum Metals Company, a wholly owned subsidiary of the Carborundum Company Construction of a plant in Akron, New York, was completed about May 1954, and the production rate reached 200,000 pounds per year in 1955. The initial price for zirconium sponge was $13.46 per pound and, under the price formula in the contract, prices in subsequent years varied from about $15 to $10 65 per pound during the five-year term of this contract Negotiations with the Foote Mineral Company for the second contract failed

HAFNIUM FOR THE MARK I REACTOR

In the first half of 1951 the Naval Reactors Program became interested in hafnium Its neutron-absorbing properties, in addition to its other characteristics, seemed promising as a control rod material The development of control rods was the responsibility of Argonne which was working on silver-cadmium rods. Admiral Rickover was interested in hafnium, but initially made sure that it remained a secondary effort Therefore, he approved only limited work to explore the properties of the material and authorized only sufficient production for developmental testing.

In July 1951 Naval Reactors' approval was obtained to fabricate hafnium control rods of the Mark I reactor design. The effort was still a backup, for the hafnium rods were to be used on a trial basis. Oak Ridge purified the hafnium-rich concentrates which had accumulated from the hafnium-zirconium separation work. The Bureau of Mines set up special equipment to process the hafnium oxide and had shipped several hundred pounds of hafnium sponge to Bettis by August 1951. Bettis ran tests that proved hafnium sponge could be made into crystal bar. A contract was placed in which Foote Mineral Company delivered about 110 pounds of suitable crystal bar in January 1952.

In December 1952 Admiral Rickover observed the results of testing the silver-cadmium control rods which were the primary design for the Mark I reactor. These results were so unsatisfactory that he made the decision not to use these rods for the Mark I reactor and immediately approved use of hafnium control rods. The Foote Mineral Company then converted additional hafnium sponge to about 3000 pounds of crystal bar, the approximate amount needed for the Mark I reactor control rods. Foote's price was about $91 per pound, based on the company's paying the Commission $45 per pound for sponge feed material. The rapid advancement of this secondary development program was shown by the decreased price. Less than three years earlier, Foote had quoted a price for supplying five pounds of hafnium crystal bar at $2000 per pound, excluding the cost of Government-furnished hafnium oxide.

The expedited program to obtain hafnium for the new rods without delaying the Mark I proved to be comparatively simple. The process development had been carried out and sufficient feed material was available in the production pipeline. Bettis received the crystal bar from the Foote Mineral Company and fabricated the material into control rods at a rate consistent with the Mark I reactor fabrication schedule. Had the development contracts not been placed when they were, the metal would not have been available in time. Hafnium became an important material for the Naval Reactors Program and, as will be noted later, posed its own set of production and procurement problems.

ZIRCONIUM FOR THE MARK II REACTOR FOR NAUTILUS

The assembled Mark I reactor was completed and shipped from Bettis to the Idaho testing station in late 1952. By that time, work on the Mark II reactor for the *Nautilus* had already begun.

Recognizing that cost savings could be realized by eliminating the crystal-bar refining steps, efforts had continued on zirconium melted directly from sponge. As a part of these efforts, steps were taken to develop the interest and capability of industrial firms in the melting and fabrication of zirconium. Arrangements were made in December 1951 with interested companies to do experimental work and make trial runs with Government-furnished sponge. The sponge was furnished at no cost to the companies; the companies made no charge to the Government for the work carried out; and the Government, principally Bettis, with some work done by the Bureau of Mines and Argonne, evaluated the samples and test results. The following companies participated in this early program:

Allegheny Ludlum Steel Corporation

Climax Molybdenum Company

Rem-Cru Titanium, Inc.

National Research Corporation

Olin Industries, Inc.

Bettis was then authorized to place orders with these companies, except for Rem-Cru which dropped out because its equipment was not compatible with zirconium processing requirements.

On the basis of experimental work done by the Bureau of Mines and Bettis, supplemented by the experience of the industrial firms, Bettis recommended and Naval Reactors approved the process utilizing arc melting of consumable electrodes made of compacts of zirconium sponge with other alloy constituents in water-cooled copper crucibles. The initial ingots would then be used as the electrodes for remelting into larger ingots. The double melting was necessary to assure good homogeneity of the alloy. In 1952 and 1953, Allegheny Ludlum, of the industrial organizations, had the best capability for this process.

Melting of zirconium alloy ingots for the *Nautilus* reactor began in September 1952. The Bureau of Mines provided the sponge and converted about 90 percent of it into ingots. The Bureau blended the sponge at Albany, Oregon, compacted it at another Bureau facility at Boulder City, Nevada, and returned the material to Albany for melting into ingots which weighed about 100 pounds. Four or five of these first-melt ingots were welded together into an electrode from which an ingot was then melted which weighed 300 to 400 pounds.

As a hedge against possible problems resulting from elimination of the crystal-bar step, a reserve of about 40,000 pounds of crystal-bar zirconium, about enough for another reactor, was accumulated from Bettis and Foote Mineral Company. In 1952 both organizations discontinued their production of crystal-bar zirconium.

Fabrication of the *Nautilus* reactor was completed in April 1954.

COMMERCIAL PRODUCTION IN 1953-1954

A major step in the development of commercial sources of zirconium and hafnium was the contract which Carborundum Metals Company had entered into on May 13, 1952, as mentioned earlier. Negotiations with the Foote Mineral Company, intended to provide a second source of zirconium, had failed at the end of 1952. However, other companies became interested in zirconium and hafnium and submitted unsolicited proposals. As a result, a new Contract Board, similar to the previous one except for some changes in membership, was established in January 1953. The Board considered proposals from Foote Mineral Company, the Air Reduction Company; Eagle-Picher Company, Horizons, Inc., National Lead Company; and Reynolds Metal Company.

The Board recommended Eagle-Picher Company because the company was willing to accept a contract essentially the same as the Carborundum Metals Company contracts, including the initial unit price of $13.46, which was more favorable to the Government than the other proposals. However, the contract was never executed because in early 1953 requirements for zirconium and hafnium were still too uncertain.

After Carborundum Metals Company had achieved acceptable production from its new plant, the Bureau of Mines began to curtail its activities. It discontinued hafnium separation work in December 1954 and zirconium sponge production in May 1955. Through process improvement and increased efficiency, the Bureau had increased its sponge capacity to about 225,000 pounds per year. It had done good work but was anxious to get out of the program. From the beginning the Bureau of Mines understood that it would be involved in production only as long as commercial sources were not available. The Bureau officials were uneasy about continuing production when Carborundum Metals Company went into operation, but were willing to continue as long as the Commission and the Navy gave assurance that the work was essential.

NEW REQUIREMENTS

The successful operation of the Mark I reactor demonstrated the validity of the pressurized water reactor concept and stimulated new requirements for zirconium. In 1954, the Naval Reactors Program was expanding to include more submarine and surface ship projects, as well as the pressurized water reactor for the Shippingport Atomic Power Station which had been assigned to Admiral Rickover by the Commission. By 1956 the estimate of zirconium required had increased to over 2,600,000 pounds per year beginning in 1959. About 75 percent of these requirements were for shipboard reactors including refueling of nuclear ships, an operation which was expected to take place every few years. The estimate also included significant amounts of zirconium for the AEC's Hanford and Savannah River production reactors and for the atomic powered airplane program.

A new factor to be considered in determining zirconium requirements was the interest of several electric utilities in nuclear powered reactor plants. Recognizing that civilian nuclear power reactor plants would be a potential source of zirconium requirements, the Commission informed the utilities of its procurement plans.

Civilian interest, however, was necessarily small at this stage and there was no intent by the Commission to procure zirconium for the utilities. Of immediate importance was the amount of zirconium required for the Naval Reactors Program. The Commission's appropriations included no funds for the continuing Navy requirements, and the Commission saw no reason why it should procure zirconium for the Navy. Until this issue was resolved, no new contracts could be placed.

The issue was critical. Admiral Rickover saw advantages to combining the requirements of both the Commission and Navy while continuing to follow Commission procurement channels. Turning zirconium procurement over to the Navy would mean disrupting the already established procedures and channels which had succeeded in reducing the cost of zirconium. This issue was settled when Admiral Rickover obtained the Navy's agreement for him to transfer Navy funds to the Commission for the purpose of procuring reactor cores.

Estimating the requirements for new long-term contracts involved obtaining information from several groups. Naval Reactors furnished dates by which various types of reactors were to be needed. Bettis provided estimates of the zirconium and hafnium needed for each type of reactor. The Pittsburgh Area Office then computed lead times and prepared production schedules. These were furnished to Naval Reactors for approval.

To meet the growing overall requirements for zirconium, the now customary procedures were followed. New proposals were solicited in November 1955, and on January 20, 1956, a Contract Board for Zirconium and Hafnium Production was established to evaluate proposals received for five-year contracts and to recommend actions to obtain the increased quantity of zirconium required. One possibility considered by the Board to meet the near-term needs was to reactivate the Bureau of Mines facility at Albany, Oregon. Admiral Rickover and I went to Albany to investigate the feasibility, cost, and schedules. However, the Commission and the Bureau of Mines were both reluctant to make this move, for such an action would imply a step backward from the goal of commercial procurement.

Contractor operation of the Bureau of Mines facilities at Albany, however, was another matter Late in 1955 the Wah Chang Corporation had proposed to enter the field by conducting a development program which would use the Albany facilities to improve the production process for zirconium and hafnium. The Wah Chang proposal was modeled on an agreement which the company had made in May 1955 to develop an improved titanium process at the Bureau of Mines experimental station at Boulder City, Nevada.

Wah Chang was a New York organization engaged in mining tungsten ores and the manufacture of tungsten carbide powder and shapes. In addition, the company had acted as an agent for the U. S. General Services Administration in purchasing tantalum and niobium ores and concentrates.

No action was taken on the Wah Chang zirconium-hafnium proposal until the long-range program could be evaluated.

In early 1956 invitations for proposals to operate the Bureau's facilities were issued. Responses were received from a number of companies, including Wah Chang Corporation, Olin Matheson Chemical Corporation, and Harvey Aluminum Division. The Harvey Aluminum proposal appeared best, but negotiations failed to remove reservations which were inconsistent with the fixed-price contract intended. In negotiations, Wah Chang revised its proposal and, on April 27, 1956, the Commission signed a contract.

Wah Chang was to deliver up to 600,000 pounds of zirconium sponge by June 30, 1958. The initial unit price was $9.39 per pound of zirconium sponge and was subject to renegotiation after the first six months of the plant's operation. However, the change in price could only be downward; actually the price dropped to $9.07 per pound. Wah Chang immediately took possession of the Bureau's plant, and by June 30, 1956, was in production.

Shortly after the contract was signed, Naval Reactors further increased its requirements for zirconium for the next 18 months. Wah Chang was asked to speed up its production. The company responded in a proposal which resulted in a contract to: (1) expand at its own expense the hafnium separation equipment in the Bureau's plant and to increase the output of zirconium sponge from 240,000 to 300,000 pounds per year with no change in unit price, and (2) build a new privately owned facility a few miles from the Bureau of Mines facility. From the new plant Wah Chang would provide an additional 270,000 pounds of zirconium sponge per year at $12.00 per pound.

Wah Chang began sponge production in its new plant in February 1957. In April 1957 a second order for 270,000 pounds of sponge was placed with the new plant. This was delivered at a price of $9.35 per pound. In March 1958 the completion date of the contract was extended to February 1959, and the price of the last 191,000 pounds reduced to $8.24 per pound.

By these agreements the Commission had been able to purchase urgently needed zirconium sponge at prices less than the $12.42 per pound concurrently being paid to Carborundum Metals Company under its existing contract, with no additional payment by the Government for facilities, and with no commitment for purchases beyond known immediate requirements.

A further source used to meet the short-range requirements was a barter arrangement. A Japanese company had successfully applied the Kroll process to titanium production. From the International Conference on Peaceful Uses of Atomic Energy held in Geneva in 1955, the company obtained information on zirconium and hafnium technology. The company offered to deliver zirconium and hafnium to the United States at prices which were approximately the same as Carborundum prices

Admiral Rickover approved an agreement with the Toyo Zirconium Company for 400,000 pounds of sponge and associated hafnium. The Commission paid dollars to the Commodity Credit Corporation, an agency of the Department of Agriculture, which in turn provided grain of equal value to the Hugo Neu Corporation, a Japanese trading company in New York, which then sold the grain in Japan for yen which went to pay Toyo for the zirconium and hafnium. Because of technical difficulties and a serious fire, the company failed to deliver the full 400,000 pounds of zirconium within the specified time. However, 325,000 pounds were received which proved to be of satisfactory quality.

LONG-TERM CONTRACTS

In February 1956 the Contract Board for Zirconium and Hafnium Production received proposals from ten companies and recommended awarding three five-year contracts with fixed prices for the first year of production, and annual price redetermination thereafter, but within a fixed price ceiling.

National Distillers Products Corporation and NRC Metals Corporation, a wholly owned subsidiary of the National Research Corporation, submitted the two lowest bids. Both proposed new process modifications. National Distillers desired to use sodium instead of magnesium as the reductant, and NRC desired to use a different solvent in the hafnium separation step. Technical teams, consisting of personnel from Naval Reactors, the Pittsburgh Area Office, and Bettis visited the companies. Upon receiving the team evaluations, the Board recommended contracts with these two companies. The Board recognized the uncertainties involved, but believed that the attractive prices justified the risk. The contracts finally placed were for the following quantities and at the indicated prices:

	Annual Delivery Rate	Unit Price per Pound, Initial Year
National Distillers	1,000,000 pounds zirconium	$4.53
	21,500 pounds hafnium oxide	2.75
NRC Metals	700,000 pounds zirconium	6.50
	15,000 pounds hafnium oxide	5.03

The National Distillers Products Corporation contract was signed May 1, 1956. The company at once began to design and construct facilities in Ashtabula, Ohio. National Distillers made its first shipment in May 1958. Using sodium to reduce zirconium tetrachloride delayed delivery because it was difficult to remove the sodium chloride from the zirconium sponge. Eventually, the problem was resolved by drip-melting the sponge. The result was a zirconium chunklet which met specification requirements.

The NRC Metals Corporation contract was also signed on May 1, 1956. NRC built a plant near Pensacola, Florida. Initial shipment of zirconium sponge took place in February 1958, but because of technical problems, NRC did not reach contract levels until a year later.

The Hugo Neu Corporation, representing the Japanese producer, submitted the third lowest bid. This offer became the basis for the barter arrangement mentioned earlier.

Horizons Titanium Corporation submitted the fourth most attractive proposal, but its process was unproven as far as zirconium was concerned, so no contract was awarded.

Carborundum Metals Company submitted the fifth best offer, judging solely by price. The Board favored Carborundum for a third contract, so that at least one of the three companies would use a proven process. The initial stumbling block was the high proposed price. The company eventually reduced its price for several reasons. First, it had not understood that its price was so far out of line. Also, during the subsequent negotiations, it was agreed that price redetermination could be upward as well as downward, a provision which made it easier for Carborundum to reduce its initial contract price.

Carborundum signed its contract on April 30, 1956, for annual delivery of 500,000 pounds of zirconium sponge at an initial price of $7.72 per pound. A new plant was built in Parkersburg, West Virginia. Nominal plant capacity was 1,200,000 pounds of sponge per year, but initially some equipment was limited to half that capacity. The Parkersburg plant was a scaled-up version of the Carborundum plant in Akron, Ohio. The company made its first delivery from the new facility in September 1957. As soon as routine production was assured, Carborundum closed down the old plant.

At the time these contracts were negotiated, it was recognized that the zirconium and hafnium being purchased by the Government would subsequently be used, as Government-furnished material, under separate contracts for fabrication of fuel elements for reactor cores. As a long-range objective, it was intended that the fuel fabricators should become responsible for procurement of raw materials so that the Government would not have responsibility for furnishing the material. To facilitate achieving this, these contracts stipulated that the Commission had the right to "allocate" the product to other designated users such as fuel fabricators. In effect, this permitted the Commission to assign to the reactor fuel fabricators its rights and obligations under these contracts to purchase from designated zirconium sponge producers material in amounts specified by the Government. When such an assignment was made, the fuel fabricator scheduled, accepted, and paid for the material. During the term of the contracts, about 30 percent of the sponge was allocated to the fabricators. As a result, the Commission took delivery and paid for only the remaining amounts. In some cases, allocation was made to melters and fabricators of zirconium who were suppliers to the fuel contractors. The allocation procedure reduced Government funds obligated and paid under the zirconium procurement contracts.

The three five-year contracts marked the final major step achieving commercial sources for zirconium and hafnium summary, about 10,532,000 pounds of zirconium sponge, 277,000 pounds of hafnium oxide, and 8000 pounds of hafnium sponge were delivered between 1957 and 1962 under the three contracts. Of this, about 3,152,000 pounds of zirconium sponge were sold under allocation to fabrication contractors, and the balance of 7,380,000 pounds was paid for directly by the Government. Government direct payments amounted to $46,729,000. If the zirconium and hafnium products are considered of equal value, the average price paid by the Government for the products delivered by these contracts was about $6.10 per pound.

HAFNIUM

Discussion of hafnium requirements has been kept separate because of the unusual problems presented by this material. As time went on, the demand estimated by Naval Reactors for hafnium increased substantially along with the increase in zirconium demand. Zircon sands, which contained only about 2 percent as much hafnium as zirconium, were the only known economic source of the metal. However, the predicted need for hafnium was greater than the amounts which would be available as a by-product from producing predicted zirconium requirements.

In 1954 the Bureau of Mines was asked to search for sands with a higher hafnium content The Bureau examined over 200 specimens from several countries, including Colombia, Ceylon, the Malay States, India, various parts of the Australian and African continents, as well as the United States Although isolated samples contained hafnium-to-zirconium ratios greater than 2 percent, no sources of higher hafnium sands of any significance were identified.

In 1956 and 1957, when the anticipated shortages appeared increasingly serious, consideration was given to using alternate control rod materials and stretching the available supply by diluting it As another measure, no hafnium was shipped to contractors which were not involved in the Naval Reactors Program Contract provisions prevented Carborundum Metals Company and Wah Chang Corporation from selling the metal to commercial customers One, a major electric utility, complained to the Chairman of the Commission that it could not get the hafnium it had ordered from Wah Chang The Chairman turned to Admiral Rickover who, since the utility had an urgent problem which required hafnium to be used, agreed to meet the request, provided the Navy did not suffer. With little further delay, the utility's need was met

Fortunately a serious shortage never occurred The growing demand of civilian power reactors for zirconium led to sufficient hafnium production to meet the needs of the Naval Reactors Program.

Each of the three five-year contracts gave the Commission the option of taking hafnium either as oxide or as sponge Oxide was chosen for all contracts because the relatively small quantities made by each contractor could not be efficiently processed into sponge. By consolidating the oxide from all three contractors and that from Wah Chang, higher yields and lower costs were realized by converting the oxide to sponge under a separate contract.

Efforts to develop a process to eliminate the crystal-bar step for hafnium never achieved success. The Commission extended the 1952 Foote Mineral Company crystal-bar contract for three and a half years. In 1955, after trying unsuccessfully to interest other companies, a new contract was negotiated with Foote. In 1959 the question again arose of extending this contract. As Foote insisted on increasing its conversion price, Admiral Rickover decided not to extend the contract.

For a while various alternative contracts were used to obtain hafnium, often with Foote serving as subcontractor. Developing a second source was not easy. Eventually, the Nuclear Metals and Equipment Corporation (NUMEC) entered the field. Organized in 1957, the company's price became competitive with Foote in the early 1960's.

GOVERNMENT INVENTORY OF ZIRCONIUM AND HAFNIUM

Since the Bureau of Mines facilities produced most of the zirconium and hafnium through June 30, 1955, the materials in process at the Bureau represented a substantial Government-owned inventory which had to be financed. By June 30, 1955, the cost of the inventory was about $7,200,000, of which about $500,000 was for hafnium. Of the zirconium cost, about $1,000,000 covered the inventory of crystal bar. The rest consisted of sponge or ingots awaiting further processing, as well as scrap.

As production by the Bureau of Mines facilities drew to a close, the in-process portion of the Government-owned inventory gradually decreased, and for a few years there was a slight decline in the inventory. Later, the inventory grew as sponge from short- and long-range commercial procurement programs was received. A factor in the increased level was the lessening of requirements because of delay in ship construction.

Inventory management and control was complicated because the materials were scattered at several locations from which shipments were made. The AEC's Chicago Operations Office had the responsibility for property management and accounting, but depended on the Pittsburgh Naval Reactors Office to implement the procedures. As the result of a review conducted in 1955, material cost values were adjusted and standardized, and Bettis took over centralized accounting and control of the zirconium and hafnium inventories. Also, certain types of scrap and off-grade materials were disposed of. An inventory write-off amounting to $4,000,000 was shared by the Commission and the Navy.

END OF GOVERNMENT CENTRALIZED PROCUREMENT

All of the three contractors, National Distillers Products Corporation, NRC Metals Corporation, and Carborundum Metals Company experienced substantial cost overruns of their estimates for facilities and start-up. In addition, National Distillers and NRC (and their successors), probably because of the untried production processes they had chosen, found their production costs higher than expected. According to information provided during the original contract negotiations, the three companies had based their prices on construction and start-up costs amounting in total to about $16,000,000. Audit information developed later showed that the actual cost could have amounted to about $36,000,000. However, the overrun did not result in any increase in price, since this type of cost was not subject to redetermination.

The major difficulties for the long-term contractors was the failure of the zirconium market to develop as expected. The development of a civilian nuclear power industry was not as rapid as hoped for by the contractors. Several assumptions on which the 1956 estimates of Government requirements had been based proved too optimistic. For example, improvements in naval reactor core lifetimes reduced the frequency of refueling ships.

Although Admiral Rickover and other Commission officials considered terminating one or more of the contracts, such action was not taken because calculations showed this not to be in the best interest of the Government. Admiral Rickover maintained that a stockpile was needed to support the future needs of the Naval Reactors Program.

When the long-term contracts expired, the contractors all appealed to the Commission, and later to Congress, urging the extension of the old contracts or the negotiation of new ones. In either case, the Government was to continue to support the industry. The political pressure fell largely upon Admiral Rickover. He maintained that there was no reason to continue the direct purchase of zirconium and hafnium because he considered the long-term contracts had adequately established the zirconium industry.

To avoid complete termination of Government purchases, he established a policy under which only 35 percent of the continuing annual requirements of Naval Reactors for zirconium would be supplied from inventory, while the remaining 65 percent would be purchased on the open market by the contractors and fabricators who needed zirconium products to manufacture naval reactor cores. For several years, these additional purchases, combined with zirconium requirements for the commercial nuclear power plants, resulted in a continuing market of roughly 2,200,000 pounds of zirconium sponge per year, the same level which had been guaranteed under the five-year contracts.

Changes of names occurred among these companies, and it is useful to summarize them here. National Distillers Products Corporation assigned its contract to the Mallory-Sharon Metal Corporation, a newly formed, partially owned subsidiary. Later in 1960 this contract was assigned to Reactive Metals, Inc., in which National Distillers had an interest. NRC Metals Corporation assigned its contract to the Columbia-National Corporation, which was jointly owned by the National Research Corporation and the Pittsburgh Plate Glass Company. In 1963 Pittsburgh Plate Glass acquired complete control of Columbia-National. The Carborundum Metals Company, after contract deliveries had been completed, assigned its contract in 1965 to Carborundum Metals Climax, Inc., a new company jointly owned by the Carborundum Company and the Climax Molybdenum Company. Two years later Carborundum sold its interest to AMAX Specialty Metals, a division of American Metals Climax, Inc. (the successor to Carborundum's first partner). Wah Chang Corporation, not one of the five-year contractors, was acquired by the Teledyne Corporation and renamed the Teledyne Wah Chang Albany Corporation.

AMAX Specialty Metals and Teledyne Wah Chang now remain as the only two major producers in the business. AMAX produces sponge at Parkersburg, West Virginia, and melts it into ingots at Akron, New York, where it also has equipment to roll plates and manufacture tubing. Teledyne Wah Chang at Albany, Oregon, has a fully integrated plant which includes the capability to melt, forge, and extrude. It also has crystal-bar conversion facilities, which eliminate the need to subcontract hafnium crystal-bar production. Wah Chang can produce some forms of zirconium and hafnium that AMAX cannot.

The year 1965 marked the end of the Pittsburgh Naval Reactors Office role in procuring zirconium and hafnium for the Government. After that time, any Commission facility needing the metals purchased its specific requirements from suppliers on a normal commercial basis.

SUMMARY

An overall estimate of all zirconium purchased and used by the Commission is as follows:

	Zirconium Sponge Weight, Pounds
Bureau of Mines production	1,000,000
First contract phase (Carborundum, Wah Chang, and Hugo Neu)	3,200,000
Second contract phase (Carborundum, Columbia-National, and Reactive Metals)	10,500,000
Open market purchases from 1965 to 1974	11,900,000
TOTAL PURCHASES, INCLUDING ALLOCATIONS	26,600,000
Inventory in 1974	2,300,000
TOTAL UTILIZED	24,300,000

The 24,300,000 pounds of zirconium sponge were used for the Naval Reactors Program, the Shippingport Atomic Power Station, the Light Water Breeder Reactor, Commission production reactors, and general development programs. Assuming that the price of sponge from open market puchases averaged $5.00 per pound, the total cost of the zirconium purchased was about $170,000,000 or an average of about $6.40 per pound.

A similar estimate for hafnium is as follows:

	Hafnium Sponge Weight, Pounds	Hafnium Oxide Weight, Pounds
Bureau of Mines production	22,600	--
First contract phase	21,000	39,000
Second contract phase	8,000	277,000
Open market purchases to 1974	328,000	--
TOTAL PURCHASES	379,600	316,000
Inventory in 1974	80,000	9,000
TOTAL UTILIZED	299,600	307,000

Since the hafnium was purchased in various forms, an average price has no significance.

Naval and civilian nuclear reactors continue to be the principal users of zirconium and hafnium. Attempts to use zirconium for piping, pump components, and other equipment in chemical processing plants have not led to many applications. New uses for hafnium, but in small quantities, include photographic flashbulbs and alloys for high-performance aircraft turbine blades. Hafnium sales now appear to be less than the amount of hafnium potentially available as a by-product from all zirconium production.

TECHNICAL DEVELOPMENT OF ZIRCONIUM FOR NUCLEAR REACTOR USE

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INTRODUCTION

This paper covers the technical aspects associated with the development of zirconium for water-cooled nuclear reactors, beginning in early 1949 when the Bettis Atomic Power Laboratory was established as a part of the Naval Reactors Program. At that time the decision had already been made by Admiral Rickover that zirconium would be the reference core structural material for the Mark I pressurized water reactor in the Idaho prototype and the Mark II reactor being built for the nuclear submarine *Nautilus*. While in the course of the next 25 years small-scale investigations were performed on other potential core structural materials such as stainless steel, niobium, aluminum, and beryllium, the pressure for continual development, improvement, and application of zirconium was predominant and unrelenting.

The reader may be impressed by the recurrence of sudden and apparently erratic shifts in materials selection, fabrication, alloying, etc. Such flexibility would have been impossible without the continuing support and emphasis by Admiral Rickover and the Naval Reactors Program on zirconium development. Thus as shortcomings of initial choices were revealed by test or analysis, a sound technical basis was available to support improved directions.

In retrospect it is somewhat of a miracle that zirconium was selected for so restrictive, demanding, and schedularly limiting an application. The corrosion resistance of the material available at that time, as will be discussed later, ranged from unacceptable to disastrous. It is ironic to reflect that, of the three

Group IV-A elements, titanium, zirconium, and hafnium, only zirconium shows this exaggerated sensitivity of hot water corrosion resistance with respect to purity and structure. In other respects the selection of zirconium turned out to pay unexpected dividends. Because of the low neutron absorption cross section, a smaller amount of uranium is required to produce a critical reactor mass; the many slip and twinning modes available lead to tough, ductile behavior under most direct or cyclical mechanical stressing conditions and make it relatively amenable to most metal fabrication methods; the high solubility for gaseous contaminants such as oxygen and nitrogen facilitates welding or solid-state bonding processes and yields microstructures singularly clean of the inclusions that plague most other commercial metals; and the low elastic modulus and low thermal expansion coefficient limit residual internal and thermal stresses, although the poor thermal conductivity with respect to the latter is unfavorable. On the other hand, the anisotropic mechanical and physical properties resulting from its hexagonal crystal structure lead to dimensional instabilities; the strength properties at even moderately elevated temperatures are by no means notable; and hot water or steam corrosion resistance can be maintained only by strict control of chemistry, processing, and environmental conditions, and even then only to modestly elevated temperatures.

ZIRCONIUM CRYSTAL BAR

The crystal-bar process (also called the iodide decomposition, the van Arkel, and the DeBoer process) had been known for approximately 50 years at the inception of the Naval Reactors Program; its early history is described in Chapter 5 of "Metallurgy of Zirconium," edited by Frank Kerze of Naval Reactors and me, and published in 1955. This process is essentially a refining rather than a metal reduction technique; zirconium tetraiodide is formed at the surface of a bed of impure metallic zirconium maintained at low temperatures (approximately 400C) by reaction with free iodine and is decomposed at the surface of a hot (approximately 1400C) filament, depositing pure zirconium on the filament and liberating iodine vapor to again react with the impure zirconium. The designation "crystal bar" arose from the bright surface and the external shape of the grains that grew on the filament. This material was commercially available in small quantities from the Foote Mineral Company, which initially utilized a rather impure sodium-reduced sponge material as the raw material for subsequent refining.

The samples of crystal bar which were initially available were customarily cut into approximately 1-inch-long segments for corrosion testing in high temperature water autoclaves. Corrosion-resistant material became black after testing while noncorrosion-resistant samples became white, the different appearances being related to the thickness and physical nature of the zirconium oxide corrosion product film. Samples showed a bewildering variety of corrosion-test behavior. Sometimes entire samples were gratifyingly black while closely adjacent samples, even from the same length of crystal bar, were white; other samples were black on the outside with a white core, and vice versa. This behavior was originally attributed to poor control of the atmosphere inside the DeBoer vessels and variation in the amount and nature of specific impurities.

A committee of scientists from various cooperating sites was charged by Admiral Rickover with the responsibility for detecting and measuring the culprit impurity elements. This committee consisted of representatives from Bettis, Massachusetts Institute of Technology, Sylvania Electric Products Company, Argonne National Laboratory, Bureau of Mines in Albany, Oregon, Battelle Memorial Institute, and Iowa State at Ames. The original conjecture concerning the role of impurity elements proved indeed to be prescient. The offending elements were soon identified. Nitrogen contamination arose from insufficient purification of the initial atmosphere or leaks that developed in the deposition vessel; this element proved to be the most insidious and damaging impurity. Titanium impurities arising from inadvertent admixture with raw titanium sponge, which was purified in the same facilities as the crystal-bar zirconium, also led to local corrosion failures. Inadvertent use of tungsten starting wire for the zirconium deposition, impurities arising from use of aluminum gaskets, etc., were other causes of the variable corrosion behavior.

From these results it was inferred that, if the refining process were conducted under sufficiently antiseptic conditions relative to impurity contamination, attainment of a reproducible high level of corrosion resistance could be ensured. Fortunately at this time a process became available for production of a purer grade of zirconium for further refining by the iodide process. Dr. William J. Kroll, who previously had developed a magnesium reduction process for the production of ductile titanium metal, was confident that the same basic methods would produce a pure zirconium sponge and oriented the Bureau of Mines work at Albany, Oregon, in this direction. In this process zirconium tetrachloride vapor, prepurified by sublimation, is brought in contact with the reductant, molten magnesium, using precautions to exclude air during all critical operations. The use of this higher purity raw material, Bureau of Mines Kroll-process sponge, greater care in evacuation and sealing of the deposition vessels, and, in general, improved operating practices and procedures by the vendor of the refined zirconium, Foote Mineral Company, soon resulted in an improved yield of corrosion-resistant product.

However, as discussed by Mr. Geiger in the accompanying paper, Admiral Rickover was unwilling to entrust so vital a portion of the Mark I nuclear reactor fabrication and performance to a single commercial vendor without the opportunity to oversee and independently evaluate his process. This led to setting up a 12-inch-diameter experimental DeBoer vessel at Bettis; the vessels used by Foote Mineral Company were smaller in diameter (9 inches) and length. The account of the painstaking engineering and scientific effort which went into this work, the material engineering and testing to select constructional materials least subject to iodine attack, the meticulous design of gasketing, electrical lead-ins, and electrical attachments to the deposition base, the analysis of the electrical voltage/current relations during crystal-bar growth, and the selection of raw sponge temperatures, iodine quantities, etc., would constitute a voluminous tale in itself and is beyond the scope of this article. In any case this facility proved capable of producing lengths of crystal bar, 7 to 10 pounds in weight, of unequalled purity and corrosion resistance. Furthermore, the availability of this facility permitted a number of questions to be answered concerning transfer of impurities from the atmosphere, the sponge, and the materials of construction.

The main value of the experimental facility was that it served as a standard for gauging the quality of the crystal-bar product furnished by Foote Mineral Company. While corrosion resistance improved tremendously over that displayed by the early product, long periods were still experienced when no material useful for Mark I production was manufactured. Vivid in the memory of many at Bettis was the failure in a corrosion test autoclave of samples from a shipment of production crystal bar from Foote. While most of us stood around the autoclave aghast at this serious setback, the head of the materials development activity at Bettis carefully ladled the white ZrO_2 corrosion product remnants of the test onto some paper towels, carried them to the office of the Bettis Laboratory Manager, and, with a ghoulish grin, said, "This is what you're going to use to build your Mark I."

The decision was therefore made by Admiral Rickover that, to meet the tight schedule and exacting quality requirements of the Mark I reactor plant, the Foote Mineral Company product would have to be supplemented by a hopefully more reproducible source of supply. He obtained Commission approval to construct a full-scale production facility at Bettis which would have the capability of producing the core material requirements for the Mark I plant. This facility was put into operation within the scheduled 16-week period from program approval to facility completion by round-the-clock, 7-day-per-week personal involvement of engineering, technical, manufacturing, production, procurement, administrative, and crafts personnel. To secure greater manufacturing efficiency, higher deposition rates, and reduction of contamination during opening and closing of the many small vessels, the diameter and length of the production deposition vessels were doubled and the weight of crystal bar produced per charge was increased by a factor of ten over that produced in the smaller vessel used in the initial experimental facility. The many other decisions made during design and construction, the many experiments performed concurrently in the experimental facility to support features of the production facility, etc., are again beyond the scope of this account. Suffice it to say, it was a proud day for the Bettis Laboratory and the Naval Reactors Program when full production was reached and the laboratory technicians could answer the laboratory phone with the grand announcement, "Crystal Bar!" Approximately 85 percent of the Mark I core was built with crystal bar manufactured by this facility, the remainder being manufactured utilizing the Foote Mineral Company product.

Lest the impression be conveyed that the Bettis crystal-bar venture was an unblemished technical success, dark clouds descended shortly after achievement of full production. Those experienced in the art and science of corrosion worried that continued purification of the product was not necessarily the correct path. Indeed, some inkling of this predicament was available from efforts that had been made to fabricate zirconium by conversion of the crystal bar to a powder and subsequently to process it by conventional vacuum-powder metallurgical techniques. In fact, initial efforts to make compacts by this method, utilizing hydriding to ZrH_2 to embrittle previously corrosion-tested crystal bar and facilitate its comminution, yielded product of disastrously poor corrosion resistance until it was found that the purest available hydrogen was contaminated with relatively high levels of nitrogen. However, even after the hydrogen was purified so that no nitrogen contamination occurred, the corrosion resistance of the sintered compacts never attained that of the starting material. It was inferred that during sintering (at temperatures well above 1000C), some as-yet unidentified impurity element whose presence was necessary to confer corrosion resistance was vaporized. In fact, for some time it was feared that melting would cause vaporization of a beneficial impurity element and that melted and fabricated crystal-bar zirconium might never attain the corrosion resistance of the initial stock. For this reason an effort was mounted to consolidate crystal bar by chopping it to fingertip size chunks and hot-pressing or hot-extruding it in graphite dies, an early application of the recently reinvented "particle metallurgy" process. Fortunately this expedient proved to be needless, as discussed later.

These premonitions were amply confirmed when the product of the Bettis crystal-bar facility began to demonstrate a cloudy gray appearance after corrosion testing, completely unlike the pure white appearance of impurity-contaminated zirconium, but on the other hand, distinctly inferior to the jet-black films formed on acceptable product. It was later found that an important contributor to the deficient corrosion behavior was the continuous improvement in the purity of the zirconium sponge manufactured by the Bureau of Mines at Albany, Oregon, which was used as the raw material. Finally, the unhappy state of affairs was reached where much of the Foote product was acceptable after corrosion test whereas a large fraction of the Bettis product was rejected; the greater the effort applied to tighten control of impurity sources, the worse the Bettis product behaved.

Bettis worked to ferret out analytical differences between acceptable and unacceptable crystal bar, both of Bettis and Foote Mineral Company origin. The results of this work coupled with known differences between the constructional features of Bettis and Foote deposition vessels (the latter being more subject to attack and hence transfer of iron, nickel, chromium, etc.), the miscellaneous observations of volatilization from powder product previously discussed, and the availability of early results from alloy-development programs soon directed the finger of suspicion toward the higher purity and lower ferrous-group element content of the Bettis product. With this information available, it was a short step to achievement of suitable yields of zirconium product from the Bettis facility by proper selection of raw sponge charges to ensure transfer of adequate iron, chromium, or nickel levels. Thus construction of the Mark I reactor was enabled to proceed essentially unimpeded by unavailability of crystal-bar stock.

Successful as this endeavor was, as extensive testing and evaluation of core product proceeded, sufficient evidence began accumulating that structural stock, even though fabricated from product that was corrosion-resistant in the crystal-bar stage, teetered on a razor's edge of acceptability. One of the more harrowing recollections of this period is the testing of some Mark I fuel elements which, after test, revealed on otherwise acceptably jet-black surfaces extensive white, blotchy, ghost-like regions that were mirror images of similar regions on surfaces of adjacent fuel elements. An intensive engineering troubleshooting campaign eventually revealed that the autoclaves in which the elements were tested and which were operated at saturation temperature and pressure were heated by electrical immersion heaters located at the autoclave bottoms. During the normal temperature control swing, boiling occurred on the heater surfaces and the steam bubbles rose through the water and bridged adjacent fuel element surfaces. Because the water used at that time was not carefully deaerated, the steam was enriched in nitrogen and oxygen and, as the final link in the chain, crystal-bar zirconium even with additives of iron, chromium, and nickel was not corrosion-resistant to nitrogen-enriched aqueous environments. This particular problem was solved, once the cause was elucidated, by proper autoclave construction and chemical control of the water purity. Another recurring annoyance was the exposure of the upper half of a crystal-bar batch or set of fuel elements to the steam phase during corrosion testing due to inadequate initial autoclave fill or leakage during tests; those portions exposed to the steam phase usually showed an unacceptable appearance because the iron-group element content necessary to maintain corrosion resistance in water is less than that required for steam-phase corrosion resistance.

Incidents such as those described above motivated a growing dissatisfaction with the continued use of crystal-bar product; not that it did not have its strong adherents. With the successful construction and operation of the Mark I reactor plant in Idaho, the proponents of this process had the powerful argument, "Why switch from a proven product to a completely unknown and untested entity such as an alloy with a less pure zirconium raw material?" Projections were prepared that, with improvements in the process, crystal-bar refining could be conducted at a cost very little greater than that for the Kroll-process sponge produced by the Bureau of Mines. It is a tribute to the vision of Admiral Rickover and his staff that the latter course, initially dubious but eventually justified, was adopted and supported in the face of this beguiling alternative. Undoubtedly influential in the decision to utilize the sponge-base material was the course of the titanium industry, which from the outset utilized this product exclusively. Thus, the crystal-bar refining process for zirconium has remained a vivid memory but became nonetheless an obsolescent side stream in the continuing zirconium development story, the next phase of which, development of Kroll-process sponge-base alloys, is discussed below.

ZIRCONIUM ALLOY DEVELOPMENT

Despite the adoption of crystal-bar zirconium as the core structural material for the Mark I reactor, an effort was instituted by Naval Reactors to develop a corrosion-resistant alloy of zirconium which could use the Kroll-process sponge directly rather than after DeBoer-process refining. The continual improvement in quality and reproducibility of the sponge no doubt played a large part in this decision. A Zirconium Alloy Corrosion Committee, established by Admiral Rickover and chaired by D. E. Thomas of Bettis, consisted of representatives of most of the sites active in zirconium corrosion investigations. These sites included Battelle Memorial Institute; Nuclear Metals, Inc.; Bureau of Mines (Albany, Oregon); and Naval Reactors. In addition to identifying many of the elements which detracted from the corrosion resistance of crystal-bar zirconium, as discussed previously, work performed under the aegis of this committee soon isolated several elements which improved the corrosion behavior of sponge zirconium to a level apparently equivalent to that of good quality crystal bar. These elements were tin, tantalum, and niobium which, in decreasing order of effectiveness, circumvented the damaging effect of the impurities present in the sponge then available. Since tin was most effective and much less of a nuclear poison than its closest rival, this element was selected for concentrated investigation. The level of addition, which at one time was as high as 5 weight percent, was gradually whittled down to 2.5 weight percent as a good compromise between corrosion resistance, strength, and fabricability. The alloy was dubbed Zircaloy, with the suffix -1 appended later, and it was adopted as the reference core structural material for the reactor plant in the *Nautilus* submarine.

Manufacturing personnel, eager to initiate fabrication of the shipboard core, began ingot melting and primary ingot fabrication development both at Bettis and at vendor facilities aimed at determining the process changes which would be required to replace crystal-bar zirconium. Concurrently samples of Zircaloy-1 were subjected to continuing long-term high temperature water corrosion testing. Unfortunately as happens so frequently in advanced research and development programs, this euphoric state of affairs soon came to an end. On reviewing the long-term corrosion data as they became available, a disturbing trend became noticeable. Instead of continuing to corrode at a decreasing rate with increasing time, as was expected of well-behaved material, the corrosion rate at a specific time (later called breakaway or transition time) increased and remained essentially constant thereafter. Furthermore, the time at which this increase in corrosion rate occurred was not greatly in excess of the time at which the sponge unalloyed with tin would begin to show white, nonadherent oxide corrosion product. Examination of the Zircaloy-1 specimens after the transition period showed that the corrosion product oxide had changed from its normal glossy-black appearance prior to transition to a thicker, tan-colored adherent layer. In fact it was suspected that the tin addition reduced the unalloyed sponge corrosion rate only to a moderate extent, the principal "benefit" of the tin addition being to improve the adherence of the corrosion product oxide. For heat transfer applications, the thermal resistance posed by the thick adherent oxide made this "benefit" of dubious value indeed.

An immediate halt was called to the further processing of core product containing Zircaloy-1 and an urgent search instituted for a fallback position. Fortunately a sufficiently active series of corrosion investigations was underway so that the search was not conducted in a complete absence of information. The prior work on crystal-bar zirconium had revealed the important effect of iron additives on zirconium corrosion behavior. A melter in the Bettis fabrication shops had melted a Zircaloy-1 ingot with the ostensibly inadvertent addition of some stainless steel. It was widely suspected that the error was less than ingenuous, the melter reasoning that, since stainless steel was widely known to be highly corrosion resistant, its addition to Zircaloy-1 could only be beneficial! Whatever the motives, the resultant material did have outstanding corrosion resistance. Experiments performed under the guidance of the Zirconium Alloy Corrosion Committee had revealed the beneficial effect of nickel additions on the high temperature (≥ 750F) corrosion resistance of zirconium and alloys of zirconium with tin at these temperatures.

Within a few days of halting Zircaloy-1 processing, an evening meeting was called by W. A. Johnson with members of his materials group at Bettis who had been active in corrosion, physical metallurgy, and processing of zirconium alloys, that is, D. E. Thomas, K. M. Goldman, R. B. Gordon, and myself. The purpose of the meeting was to chart a course of action. It was unanimously agreed that to continue with Zircaloy-1 would be technically disastrous. Equally unanimous was the judgment that minor variations from the Zircaloy-1 composition would not only confer major corrosion improvements but also permit carry-over of the fabrication experience accumulated with Zircaloy-1.

The iron content of the alloy was set at a nominal level of 0.15 percent, primarily in consideration of the range of iron levels present in the various grades of Kroll-process sponge and the beneficial effect of iron additions in crystal-bar zirconium. A nominal nickel level of 0.05 percent was selected because of the beneficial effect of this additive on high temperature corrosion resistance. Chromium, which was beginning to appear as an impurity in sponge because of the use of stainless steel reaction vessels, was known to have a phase diagram with zirconium similar to that of iron and hence could be expected to behave similarly when alloyed; its content was set at 0.10 percent nominally, intermediate between the iron and nickel contents. Greatest difficulty was experienced in securing a consensus on the proper level of the tin addition. It was desirable to retain the 2.5-percent tin level of Zircaloy-1 to maintain the tensile properties at levels attractive to mechanical designers. On the other hand, because of the progressive deterioration of high temperature corrosion resistance with increasing tin additions, a strong sentiment existed to reduce tin levels to 1 percent or less. A nominal tin level of 1.5 percent was finally selected as probably exhibiting, with the 0.3-percent additions of iron, chromium, and nickel, tensile properties equal to those of Zircaloy-1, and adequately improved high temperature steam corrosion resistance. Thus at the conclusion of the evening meeting, a tentative composition for the alloy Zircaloy-2 had been selected.

On August 28, 1952 the reasoning underlying the tentative selection was reviewed with Admiral Rickover. A final composition was chosen and approved by him for use in the shipboard core, without the alloy ever having been melted and fabricated, much less tested. Aside from subsequent imposition of compositional ranges based primarily upon fabrication feasibility, the composition set in those meetings has persisted to the present. It is doubtful that, within the family of such alloy additives as tin, iron, chromium, and nickel, a different composition would be selected were the evening meeting to be repeated today.

Aside from the initial bitter complaints of manufacturing personnel who predictably denounced the alloy as being unmeltable, unworkable, and unusable, Zircaloy-2 was satisfactorily produced for the *Nautilus* reactor plant and has remained to this day the workhorse zirconium alloy, not only for the Naval Reactors Program but also for civilian water-cooled reactors. Not the least of its attributes has been the reproducibility of its properties and its insensitivity to the normal variation and accidents of quantity production.

Satisfactory as the performance of Zircaloy-2 had been, the fear grew that, with the increase in reactor core lifetimes, with the elevation of plant operating temperatures, and with the unknown but certainly detrimental effect of deposition of reactor plant corrosion products on fuel element surfaces with a resultant elevation of surface temperatures, the detrimental effect of the high tin content of Zircaloy-2 would eventually reveal itself. In cooperation with the Zirconium Alloy Corrosion Committee, experiments were conducted to determine the minimum tin content which could stabilize corrosion resistance against the nitrogen levels in the then available sponge (as well as tramp nitrogen picked up in melting and fabrication). An alloy with sponge zirconium consisting of 0.25-percent tin and 0.25-percent iron was recommended by Bettis in October 1955 as the most corrosion resistant composition in the Zircaloy family of alloys. This alloy, optimized for high temperature water corrosion resistance, was denoted Zircaloy-3 and was approved by Admiral Rickover in 1955 as the reference structural material for use in a replacement core for the prototype plant which had operated with the Mark I reactor.

Once again calamity struck and this selection proved to be abortive. Shortly after production of fuel elements for this prototype reactor core was initiated, there was noted, superimposed upon the black glossy surface of the corrosion-tested fuel elements, a network of fine white corrosion indications approximately 1/8 to 1/4 inch in length running parallel with the fabrication direction of the cladding. Microscopic examination revealed that these indications coincided with microscopic stringers of Fe-Zr intermetallic compounds which were clumped rather than being uniformly dispersed in the matrix. The poor corrosion resistance of the intermetallic phase had been well-known, but its aggregation into stringers was unexpected. This was later traced to fabrication of the material in the two-phase, alpha-plus-beta region which exaggerates the agglomeration of the intermetallic phases. Since there appeared to be no logical reason why such stringers should not appear in Zircaloy-2 as well, a close examination of the latter was performed. Predictably stringers were detected both microstructurally and by corrosion test. The better background corrosion resistance of Zircaloy-3, however, made the stringers more marked upon visual examination after corrosion testing than in the case of Zircaloy-2. It was found that associated with the stringers of intermetallic compound were strung out bubbles of noble gases, the presence of which also contributed to the rejectable appearance. Zirconium alloy melting was then performed in an inert gas atmosphere of 5 parts of argon to 1 of helium. With the increased proficiency and efficiency of melt shops and the corresponding increase in melting rates and the size of ingots, bubbles of noble gases became entrapped in the ingots and were strung out as fine bubbles during fabrication of the ingot to final shape and size. The inert gas bubble surfaces acted as interfaces for nucleation and precipitation of the intermetallic phases upon cooling from elevated temperatures at which these phases are more soluble. Experiments were performed in which the size and location of such gas-filled bubbles were measured as a function of time at elevated temperatures approaching the melting point of zirconium. These were probably among the earliest experiments on the mobility of inert gas bubbles, a subject of future importance in the behavior of nuclear fuels.

The formation of stringers could thus be avoided by appropriately altering fabrication temperatures, reducing melting rates, and taking pains to prevent incorporation of noble gases in the ingots. Furthermore, at this time vacuum arc melting of zirconium alloys became standard practice in the industry and the stringers vanished as completely and suddenly as they had appeared. However, an aura of disillusionment and disenchantment thereafter clung to Zircaloy-3, and aside from its application in the one prototype reactor, it was relegated to a fossil fate like its crystal-bar predecessor. The lower mechanical properties of this alloy compared with Zircaloy-2 also contributed to its abandonment In any case the failure of Zircaloy-1 and Zircaloy-3 contributed to the folklore that only even-numbered Zircaloys are viable and led the Naval Reactors Program community to await the development of Zircaloy-4 with considerable hope and anticipation. Before embarking upon this latest chapter in the Zircaloy family story, a digression to the discovery of the effects of hydrogen is necessary.

The synergism of the codevelopment of zirconium and titanium is no better illustrated than in the elucidation of the effects of hydrogen on the mechanical properties of these metals. In the course of a program of measurement of the mechanical properties of zirconium alloys, notched-bar impact testing was initiated. The behavior of the samples in these tests was completely unpredictable, sometimes high toughness values being obtained and at other times low values, even from samples cut from the same stock of material. Furthermore, low temperature heat treatments could radically alter the behavior. Microstructural examination revealed crystallographically oriented platelets in those samples with low impact values, and a corresponding absence of this microstructural feature in the normally behaving samples. In discussions with personnel at Battelle Memorial Institute active in titanium technology, it was determined that similar microstructural features in titanium had been identified as a hydride phase. Analysis of zirconium alloy specimens soon showed the interrelation between hydrogen content, appearance of the hydride phase, solubility and retention in solid solution upon quenching, and embrittlement in notch impact tests. Similar tests on titanium at Battelle also revealed embrittlement as a result of hydride precipitation.

The far-reaching effect of hydrogen on the mechanical properties of zirconium and its alloys gradually became ever more evident. It had been a continuing puzzle why a metal of such high apparent ductility as zirconium should fail in tensile tests, not with the typical cup-and-cone fracture characteristic of ductile materials, but rather with a spongy fracture even after considerable prior uniform elongation and reduction of area. By vacuum-annealing specimens of zirconium to reduce the hydrogen content to 5 ppm or less and then quenching from elevated temperature to liquid nitrogen testing temperatures to retain this minor level of hydrogen in solution, material was produced which had a normal cup-and-cone fracture. The same material tested at room temperature showed a spongy fracture which was found to be caused by cavitation in the necked portion of the tensile specimen resulting from the formation of voids at hydride platelets either thermally precipitated or formed during plastic straining.

Once the mechanical property deterioration was traced to hydrogen, the horrible suspicion arose that hydrogen was incorporated into Zircaloy-2 during corrosion testing. These fears were soon confirmed, approximately 50 percent of the hydrogen evolved during the reaction of Zircaloy-2 with water being incorporated into the metal. This finding, together with the observation that the material became ever more embrittled the higher the hydrogen content, threatened to set a limit to the permissible exposure of Zircaloy-clad materials much more restrictive than that posed by the formation of the external corrosion product oxide. The question was raised (and this in the days before the development of fracture mechanics technology) of how much of the embrittling hydrogen could be tolerated before endangering the safe operation of zirconium reactor cores.

This problem was exacerbated by the results of Bettis tests in 1956 of Zircaloy-2-clad uranium oxide fuel rods which were being developed by the Naval Reactors Program for the Shippingport Core I pressurized water reactor. The tests were performed in the NRX reactor at Chalk River, Canada, in high temperature water loops built by Bettis. A number of these fuel rods failed prematurely by local formation of almost solid hydride phase through the entire cladding thickness, so-called gross hydriding failures. Furthermore, at other locations in unfailed as well as failed fuel rods, the hydrogen was found to be concentrated at the external, colder surface indicating that it had migrated down the thermal gradient. The localized gross hydriding type of failure is now believed to be primarily a function of fuel operation rather than directly a consequence of Zircaloy-2 exposure.

By controlled out-of-pile thermal gradient measurements and application of the methodology of the irreversible thermodynamics, prediction became possible of the effects of thermal gradient diffusion on the concentration of hydrogen at external surfaces. By subtracting the thickness of cladding thus converted to hydride, the level of hydrogen which could be tolerated on heat transfer surfaces was determined. On nonheat transfer surfaces, the tolerable level of hydrogen was set at 250 ppm, based more on judgment than factual data. The level of hydrogen in failed fuel rods in the tests in the NRX water loops at locations remote from the failures corresponded to this level, and hence it was judged that this was the highest level which could be justified by test as being tolerable without causing fuel element failure. A somewhat more satisfactory justification of this critical hydrogen level was found in the observation that, at 250 ppm of hydrogen, Zircaloy-2 loses at room temperature its ability to neck down in a tensile test. Here again these arbitrary limits have been replaced by technically more satisfying fracture mechanics considerations.

An uneasy truce had thus been struck with the phenomenon of hydrogen absorption. If the hydrogen absorption capabilities of Zircaloy-2 structures could be predicted from knowledge of corrosion kinetics, the adverse effects of hydrogen absorption could at least be anticipated and used to set thicknesses of core structures or reactor core lifetimes. The first indications that such predictions could be faulty occurred as a result of experimentation with a new type of fuel element bonding process called "eutectic diffusion-bonding," which was being investigated as a means of fabricating plate oxide fuel elements for Shippingport PWR Core II. In this process, thin coatings of nickel, copper, or iron were applied to the surface of Zircaloy-2 components at the locations where bonds were to be made. The faying components were then heated to a temperature above the eutectic temperature of zirconium with the particular element. The formation of the eutectic caused brazing of the faying surfaces. Upon holding at temperature, the element used for surface coating diffused into the interior of the cladding, causing solidification of the braze and a solid phase bond enriched in the bonding element. On exposure of samples thus fabricated in in-pile as well as out-of-pile corrosion facilities, completely unanticipated levels of hydriding were encountered, particularly in samples bonded using nickel. The pickup of hydrogen, rather than being 50 percent of the hydrogen produced in the corrosion reaction, could be as much as 300 to 400 percent of this amount.

This finding of course called into question the entire basis which had evolved for predicting hydrogen absorption. By operation of some mysterious mechanism, the hydrogen evolved during the corrosion reaction had been tacitly tagged as being more susceptible to absorption in the metal than hydrogen dissolved in the autoclave, in-pile loop, or reactor water. Thus, for example, the hypothesis at one time was propounded that oxygen diffused through the zirconium oxide corrosion product film as a hydroxyl ion, thus nicely accounting for the 50-percent pickup of corrosion-produced hydrogen by Zircaloy-2. Contradictory observations such as the drastic reduction of hydrogen absorption in improperly deaerated autoclaves were in general ignored. However, the fact that hydrogen absorption in nickel-enriched Zircaloy-2 could be increased to well over 100 percent of corrosion-produced hydrogen effectively eliminated the peculiar significance of this source of hydrogen. In zirconium corrosion literature, reference can still be found to "percentage of corrosion-produced hydrogen" because of the convenience of this usage.

In 1958 when it was recognized that nickel enrichment of Zircaloy-2 caused the protective corrosion product film to become more permeable to hydrogen dissolved in the water or steam environment, the obvious corollary immediately came to mind that the hydrogen absorption of Zircaloy-2 might be reduced by the elimination of the intentional 0.05-percent nickel addition. Some experimental Zircaloy-2 ingots were fabricated without nickel additive and corrosion tests revealed that hydrogen absorption was indeed reduced by more than a factor of two. This alloy was then adopted as the reference cladding for the second (plate oxide) core of the Shippingport reactor, production quantities of the material were processed, and a large fraction of the core was indeed fabricated with it.

Benefiting from previous experience with the hasty adoption of new Zircaloy compositions, the proponents of this alloy formulation did not rush into its numerical designation but referred to it as "Nickel-Free Zircaloy-2" and awaited the inevitable dropping of the axe. The denouement was not long in coming. Experimenters at General Electric (San Jose), in testing the alloy for steam-cooled applications, rejected it as having inadequate steam corrosion resistance. This result could have been predicted since, as you will recall, the nickel addition was originally made to enhance high temperature corrosion resistance. It was deemed undesirable to adopt for widespread application an alloy with the stigma of reduced steam corrosion resistance. Again the pressure of cladding procurement for PWR Core II obviated the possibility for any large-scale development program. Therefore it was decided that the most expeditious means of restoring some amount of the decreased steam corrosion resistance while still retaining reduced hydrogen absorption was to raise the iron level. Since nickel forms the intermetallic compound Zr_2Ni and iron, $ZrFe_2$, a given weight of nickel was judged to be twice as effective in intermetallic compound formation as that weight of iron. Thus keeping constant the total volume of intermetallic compound, the decision was made to compensate for the loss of 0.05-percent nickel by increasing the nominal iron composition about 0.1 percent to 0.18-0.24 percent. The chromium and tin compositions remained unchanged. This alloy, which was approved by Admiral Rickover in 1960 for extensive testing and eventual use in shipboard cores, was called Zircaloy-4. It was found to retain almost as good steam corrosion resistance as Zircaloy-2 while exhibiting one-half the hydrogen absorption. This alloy has recently been adopted by the Naval Reactors Program as well as by pressurized water civilian reactor core builders as the reference core structural material.

This brings up to date the history of the Zircaloys as perceived from the vantage point of a participant in their development. As discussed in the introduction, the availability early during this history of high quality zirconium sponge undoubtedly guided the development toward use of sponge-base alloys and away from the crystal-bar base alloys utilized by the USSR in water reactors. An example of the manner in which the nature and quality of the raw material can affect the course of alloy development is well illustrated by the experience with zirconium sponge manufactured by the Columbia-National Corporation during the period 1959-1960. The corrosion resistance in steam testing of Zircaloy-2 ingots fabricated from this material never could be brought to the level of that made from Kroll-process sponge by other producers, even though the purity of the former equaled or exceeded all specifications. Small additions of silicon to the former were found to produce Zircaloy-2 of acceptable corrosion resistance. This experience illustrates graphically that the alloy formulations developed depend not only upon the application but also upon the nature of the raw material.

CONTROL ROD DEVELOPMENT

With the continuing production of zirconium for the Mark I prototype submarine reactor plant, stocks of hafnium salts of low zirconium content (about 5-percent zirconium) began to accumulate. The natural question raised was whether the reduction process (oxide to sponge to crystal bar), which had proven so successful for zirconium, was applicable to hafnium and whether the resultant product was useful in naval nuclear reactor applications, specifically as a neutron absorber for control of the nuclear reaction. Finally, A. Radkowsky of Naval Reactors and W. A. Johnson and S. A. Krasik, the latter the head of the Bettis Physics Department, decided to take some definitive action. They arranged to procure some metallic hafnium and perform physics, corrosion, and fabricability tests. This was done almost surreptitiously since the lead responsibility for the development of the Mark I control system had been assigned, under the direction of Naval Reactors, to the Argonne National Laboratory. The reference control rod material was a silver-cadmium alloy sheathed in stainless steel. Although an elaborate and apparently quite satisfactory fabrication scheme had been evolved for the control rods, continuing problems with the design, construction, materials selections, and testing of the initial Mark I control mechanism cast a pall of suspicion on all related aspects.

This problem came to a head at a meeting at Bettis the week of December 15, 1952, with Argonne and Naval Reactors personnel to review the status of the entire Mark I control problem. Coincident with this meeting, some stainless steel-clad silver-cadmium control rods fabricated by Argonne were being tested in high temperature water autoclaves at Bettis, and arrangements were made to remove the rods from test the morning of the meeting so that they could be reviewed by the visitors. The worst fears of those working on the control system were realized. Close examination of the rods revealed locations where the stainless-steel sheath appeared to be slightly raised and pulled away from the silver-cadmium core. This would of course be disastrous, since further ballooning of the sheath could cause binding of the control rod and endanger safe and controllable reactor operation.

During one of the meetings to review the status of this work, Admiral Rickover, using a plumber's tactic, hit a piece of this material with a hammer and the clad split off the base material. This result clearly indicated to him the unacceptability of this design and he at once made the decision to shift to unclad hafnium control rods as the replacement reference design for the Mark I reactor, using the crystal-bar zirconium development facility on a crash basis to make the first crystal-bar hafnium. The results of the initial tests had revealed that hafnium was much less subject than was crystal-bar zirconium to deterioration of its corrosion resistance. Not only were the normal impurities such as nitrogen less harmful, but also the absolute corrosion rate was much less at the same exposure conditions. The neutron absorption cross sections as a function of neutron energy, the absorption characteristics as a function of lifetime, and the chemical nature of daughter products matched pressurized water reactor requirements even better than did the silver-cadmium control rods. The experience on reduction, purification, and fabrication accumulated with crystal-bar zirconium was directly applicable to hafnium. Therefore the transition was made readily to crystal-bar hafnium for Naval Reactors applications.

For a time from 1950 to 1958, when almost all hafnium-separated zirconium was being used in the Naval Reactors Program, a hafnium shortage was threatened. This temporary shortage of hafnium was overcome by strict economy in use of the material. All of the souvenir hafnium paperweights, name markers, and trophies which had accumulated on engineers' and administrators' desks were collected, and these constituted a not inconsequential contribution to the hafnium supply. As zirconium was applied to more and more commercial reactors in which hafnium control rods were not used, the hafnium supply situation has considerably eased and no shortages have recurred. Crystal-bar hafnium has retained its unique primacy for this application.

CORROSION TESTING OF REACTOR CORE COMPONENTS

From the preceding account of the development of the Zircaloys from the earliest available crystal-bar samples, the reliance upon high temperature water corrosion testing to assess the quality of raw materials and finished components is probably understandable. The author once strongly advocated accepting a product based upon composition alone. However, the occurrence of stringer corrosion illustrated the danger in this approach and supported the prudence of either corrosion testing or performing some test simulating corrosion exposure for zirconium components which are required to operate under conditions approaching the lower limits of corrosion acceptability. On the other hand, as anyone familiar with specification or acceptance testing can testify, there is a great danger that the testing itself becomes the object, rather than use of the test results to ensure maintenance of material quality. Corrosion testing of zirconium has not proved to be immune from this danger, and the Naval Reactors Program has directed considerable effort toward ensuring that corrosion testing yields reproducible results and accurately reflects material quality.

In the early 1950's when corrosion testing was first applied to the crystal-bar zirconium components of the Mark I reactor, the complaint was often heard that the life of the reactor core was being used up in testing. This statement was made only partly in jest, since, although the design life of the Mark I reactor was relatively short, the life of the Zircaloy components was considered to be fixed by the time at which the zirconium oxide corrosion product reached its transition thickness and began to flake.

To permit evaluation of corrosion quality, a sensitive method of evaluating test results was necessary. Corrosion weight gain, useful in research and development tests, was of doubtful applicability since the variability among various ingots, heat treatments, and surface finishing practices would require the imposition of limits so relaxed that defective material might pass the tests. Furthermore, weighing of large components with sufficient precision to detect local deficiencies in corrosion quality was impractical. Therefore, a visual inspection method was adopted whereby the appearance of the corrosion product on the material or component is compared with that on an acceptable standard. To aid the inspection, the use of a "black box" was instituted, which is simply a standardized means of eliminating extraneous reflections, etc., from the surfaces being viewed. Under such viewing conditions, differences in materials can be detected which are beyond the sensitivity even of accurate weight change measurements.

ZIRCONIUM HANDLING AND SAFETY

Zirconium is normally characterized in metallurgy texts as one of the reactive metals. The truth of this characterization was no better emphasized in the Naval Reactors Program than in 1955 on the day of the "Great Zirconium Fire" at Bettis. In the course of construction of the Mark I and subsequent reactor plants, a large amount of zirconium machining chips, unused sponge, discards, rejects, etc., was accumulated. Because of the high cost of the hafnium separation during zirconium production, this scrap material was deemed valuable since, even if converted back to oxide and recycled, its reuse would greatly reduce the cost of zirconium. The Commission stored this scrap in concrete block bins in a storage yard at Bettis until procedures for its reuse could be developed.

On the day of the fire, one of the barrels of chips was ignited, presumably as the result of welding operations in an adjacent area. The ignition spread to adjacent bins and soon the entire Bettis site was bathed in an eerie light like that of a continuous and powerful flashbulb. I recollect that I was interviewing a prospective employe at the time. Since I had no idea what was going on, leaning on the principle of "need to know," I ignored the loud clanging of fire bells, hooting of signals, and general frantic activity. As I escorted him out of the plant, the fine white particles of ZrO_2 falling gently upon our heads, he declined our employment offer and, while conceding that Bettis would be an exciting place to work, expressed the desire for a more settled environment.

This incident, coupled with a similar fire at Oak Ridge, led to the formulation by the Commission of safe handling practices for zirconium which have been successful in preventing any chemical reaction incidents in prime contractor or vendor locations handling zirconium.

The reactive nature of zirconium once again became of concern at the time the Shippingport PWR Core I reactor was approaching its installation and initial operation. Zircaloy-2 was used extensively as the fuel element cladding as well as the core structural material. The chemical energy of combustion of the Zircaloy-2 as well as subsequent reactions of the released hydrogen, could, if released during a postulated reactor accident, cause extensive damage to the reactor containment structure. The specter was raised of violent explosions which had occurred in some titanium arc-melting facilities as a result of puncturing the crucible and contacting the molten metal with water. The Shippingport reactor, as the forerunner of commercial pressurized water reactor plants, served as the progenitor for many of the safety and safeguards practices and analyses which have subsequently been applied to commercial reactors.

The question was raised of whether ignition of Zircaloy, even if locally initiated, could spread in an uncontrollable manner to a major fraction of the Zircaloy contained in a core. The accident conditions under which such a reaction was considered most likely to occur would result from the loss-of-coolant accident in which one of the main coolant pipes would suffer a guillotine break. It was considered that, if it could be shown that Zircaloy-2 reacted with water in a predictable manner at all temperatures up through its melting-point, this should assuage fears of the occurrence of unpredictable and uncontrollable reactions. The magnanimous time period of three weeks was allotted for this demonstration. Thus, an experiment was devised in which samples of Zircaloy tubing similar to those used in Core I were heated inductively while immersed in water and the released volume of hydrogen collected and used to monitor the rate of the reaction. Barricades were set up around the water container and a system of mirrors devised so that an engineer could control the metal temperature in the course of the reaction while another engineer observed the change in hydrogen volume with time as the hydrogen bubbled up through the water column. Temperatures were gradually and progressively increased in consecutive experiments until, as the grand finale, Zircaloy was melted under water and the amount of reaction monitored during melting. These experiments, completed during the required time period, demonstrated that the occurrence of high temperature reaction rates could be extrapolated from those measured at lower temperatures, and that no new or unexpected phenomena intervened which would endanger reactor plant safety. Crude as these initial experiments were, the kinetic data derived from them and the conclusions drawn have been supported by subsequent experiments and analyses.

ZIRCONIUM FABRICATION TECHNOLOGY DEVELOPMENT

The mutually beneficial effect of the codevelopment of zirconium and titanium is again illustrated by the rapid progress made in the fabrication technology of these metals. Because of the wide range of applications which were being explored for titanium alloys, fabrication technology was most rapidly advanced by the titanium industry. However, the stringent corrosion, homogeneity, and purity specifications required for zirconium alloys led to melting, welding, and fabrication practices for zirconium which were accepted with profit by the titanium industry.

The earliest efforts were directed towards methods of melting zirconium, first crystal bar and then Zircaloy-2. Vacuum induction melting in graphite crucibles was operationally successful; however, the resulting carbon pickup was disastrous to the corrosion resistance of crystal-bar zirconium. A minor effort was then directed toward finding crucible materials which were inert to molten zirconium, a task which soon proved to be fruitless. As previously discussed, even solid-state compaction by hot-pressing was at one time seriously considered for the production of crystal-bar zirconium.

However at this time, attention was directed toward nonconsumable electrode inert-gas arc melting, a rather venerable concept which had most recently been revived for melting of the refractory metals, molybdenum and tungsten. Once the means of purifying the inert gas of oxygen and particularly nitrogen had been worked out, the art of fabricating water-cooled copper crucibles which would not spring leaks evolved, the method generated of controlling water flow to prevent formation of hot spots, and melting rates correlated with metal feed rates, ingots of crystal-bar zirconium were produced with high yields, which retained the corrosion resistance of the feed stock. These ingots, each weighing 35 pounds, were used in the fabrication of fuel elements for the Mark I core.

These ingots suffered from a lack of homogeneity; thus, local inclusion of a poorly corrosion-resistant piece of crystal bar, or, failure to secure local alloying when melting of sponge began, often resulted in rejection of an entire ingot. It was necessary to then fabricate the ingot, chop it to feed stock, and remelt it using an inert electrode. A far more satisfactory procedure was soon evolved in which the inert-electrode first-melt ingot was made the consumable electrode for a second melt, thus improving the homogeneity without incurring the costs and delays of fabricating the first ingot to feed stock size.

The final development consisted of discarding the inert electrode, which led to local contamination with tungsten, and replacing it with a consumable electrode made of cold compacted sponge with suitable addition of alloying elements; this first melt then formed the consumable electrode for the second melt. This practice was developed at Bettis and soon became the standard practice throughout the zirconium and titanium industries.

As previously discussed, difficulties began to be experienced at this time with the inclusion of noble gas bubbles and intermetallic compound stringers in the ingots. Fortunately the practice of vacuum arc-melting had become widespread in the titanium industry and proved to be transferable to Zircaloy melting. Vacuum double consumable arc-melting thus has become the established reference melting practice for zirconium alloys. Progress since then has been in the direction of increasing ingot sizes. From the 35-pound ingots fabricated for the Mark I core, melting has progressed today to 3000-pound ingots, with resulting improvements not only in yield, efficiency, and reproducibility, but also homogeneity.

Concurrently with the development of melting practices, the applicability of almost all metal-working practices has been explored either at the Naval Reactors Program prime contractor laboratories or at vendors' plants. Zirconium, and later the Zircaloys, have proven to be adaptable to fabrication by rolling, forging, extrusion, or wire-drawing. The first large scale manufacture of Zircaloy tubing was initiated in 1955 for fabrication of the Shippingport PWR Core I blanket. Seamless tubing was manufactured from extruded hollow billets either by successive stages of cold-drawing and annealing or by tube-reducing to final size; tubing of each type was included in the first Shippingport reactor core.

Active programs were also initiated on joining methods. The applicability of tungsten-inert-gas (TIG) and consumable metal electrode-inert gas (MIG) arc-welding processes was rapidly explored. The necessity for maintaining atmosphere purity in order to prevent contamination led to the development of controlled atmosphere weld boxes of unique design rather than use of shielded arcs as in other less critical applications. Again, zirconium and its alloys were found to be highly weldable and, to a large extent, immune to weld cracking. One limitation to post-welding heat treatment was encountered unexpectedly in the welding of fuel elements for the Shippingport PWR Core II reactor, a plate oxide reactor in which TIG welding was extensively used. When the plates were annealed at 1450F after welding, the customary practice at that time, and then corrosion tested, cladding cracks were detected associated with the weld regions. Metallographic examination at first revealed no structural reason for the cracks; however, more careful examination revealed that exaggerated grain growth had occurred in the welds as a result of the annealing operation, and that cracking had occurred as a result of precipitation and subsequent cracking of brittle hydride plates across the large grains. Since then, annealing temperatures of weldments have been controlled to prevent exaggerated grain growth. Electron beam welding has also been used to advantage in zirconium technology, although care has to be exercised to prevent excessive evaporation of tin, iron, and chromium from the weldments.

Joining by brazing has found little application in the Naval Reactors Program. Zirconium-beryllium eutectic alloys for brazing were developed by Bettis and found to exhibit good corrosion resistance. This technology has been applied by the Canadians in fabrication of fuel element supports for their heavy-water reactors.

A dramatic illustration of the unforgiving nature of zirconium when its reactive characteristics are ignored was afforded by the corrosion behavior of some critical zirconium components which were fabricated at elevated temperatures encased in a hermetically sealed steel sheath to prevent atmospheric contamination and resulting corrosion deterioration. Surprisingly, high levels of contamination were found on the zirconium surfaces after removal of the sheath. It was soon realized that the partial pressure of the nitrogen impurity in steels was sufficiently high and its diffusion rapid enough at fabrication temperatures to contaminate the zirconium and to reduce its corrosion resistance drastically. An enamelling steel, Ti-Namel, in which the nitrogen impurity is stabilized in the steel by titanium additions, was therefore adopted as the sheathing material for this application.

EPILOGUE

This account has traced the author's recollections of the early development of zirconium from the time Admiral Rickover selected it as the structural material for water-cooled submarine reactor cores to the early 1960's when the zirconium alloy metallurgy was firmly established and attention was concentrated on developing its potential more fully as an engineering material. Continuing support of an active development program, faith in the eventual solution of what appeared at the time insurmountable problems, and a willingness to take unconventional and bold approaches all characterized this early development period.

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