The influence of the impurity content and cooling rate on the microstructure of Zircaloy-4 nuclear fuel cladding.

Vo. Quach
University of Windsor

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LA THÈSE À ÉTÉ MICROFILMÉE TELLE QUE NOUS L’AVONS RÉCEUE
THE INFLUENCE OF THE IMPURITY CONTENT AND COOLING RATE
ON THE MICROSTRUCTURE OF ZIRCALOY-4
NUCLEAR FUEL CLADDING

by

Vo Quach

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of Engineering Materials
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science
at The University of Windsor

Windsor, Ontario, Canada
(C) 1983
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Finally, I would like to thank the Natural Sciences and Engineering Research Council of Canada for their financial/support through a research grant (No. A4391) to Dr. D.O. Northwood.
ABSTRACT

Commercially produced Zircaloy-4 fuel cladding with a range of (C+Si+P) impurity contents has been exposed to a simulated brazing treatment in the β-phase field at 1100°C for 5 minutes. The microstructural features including type of microstructure, grain size (GS), plate width (PW) and plate length (PL) obtained at room temperature after cooling from 1100°C at various rates have been measured and correlated with the impurity (C+P+Si) content. High impurity contents promote the 'basketweave-type' of α-Widmanstatten structure over the parallel-plate type of structure. The higher impurity content also gives rise to a smaller prior-β grain size and finer plates in the α-Widmanstatten structure. An increased cooling rate gives a greater percentage of the 'basketweave-type' microstructure, a smaller prior-β grain size, together with narrower and shorter plates. Furthermore, when the (C+Si+P) content is low and the cooling rate is fast, there is a martensitic structure formed which is coarser and more abundant the lower the impurity content and the faster the cooling rate. In order to isolate the influence of the phosphorus content, a series of Zircaloy-4 melts was made with approximately constant C+Si+O+N contents but varying amounts of P from 42 ppm to 160 ppm. Phosphorus is found to inhibit the growth of prior-β grains by 'pinning' with the phosphorus-containing second-phase particles. These phosphorus-containing particles acted as the nucleation sites for promoting the 'basketweave-type'
structure. This structure could not be formed without phosphorus being present. Empirical equations are developed to correlate the microstructural features with the impurity (C+P+Si) content, phosphorus content and cooling rate.
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CHAPTER 1

Introduction

Zircaloy-4 is a zirconium base alloy with additions of 1.20-1.70 wt% Sn, 0.18-0.24 wt% Fe and 0.07-0.13 wt% Cr plus impurities. Zircaloy-4 has a material with low capture cross-section for thermal neutrons, adequate mechanical properties (e.g., creep resistance, ductility, high strength to weight ratio) and good corrosion resistance in pressurized heavy water at temperatures up to about 400°C, and has therefore become adopted as the main fuel-cladding material for CANDU-PHW (CANadian Deuterium Uranium-Pressurized Heavy Water) nuclear reactors.

In Canada, the CANDU-PHW reactor is a fission heat type nuclear reactor and its fuel (natural uranium) is domestically produced. The functions of the fuel-cladding are to safely contain the radioactive fission products from the sintered fuel pellets of the high density uranium dioxide (UO₂) and to ensure the geometry of fuel bundle is maintained when the fission heat is produced and the coolant (D₂O) flows over the surface of the fuel elements.

Before fuel elements are assembled into fuel bundles, the appendages (spacers and bearing pads) are induction brazed onto the thin-walled (0.4 mm) fuel-cladding. These appendages perform two functions: the spacers maintain a distance between adjacent fuel elements, while bearing pads provide a surface on which the bundles slide within the pressure tube. A Zr-Be alloy is deposited on the pad and
allowed to react with fuel-cladding tube in situ during the brazing cycle. Zr-Be was selected as the brazing alloy because of its acceptably low fusion temperature and good corrosion resistance. The brazing cycle used to attach the appendages consists usually of 40 to 60 seconds in a glass vacuum chamber to temperature over 1000°C followed by cooling in an inert gas atmosphere (1). Due to the brazing process up to 30% of the length of the fuel-cladding is affected by the heat (2) and the result is the formation of either a basketweave or a parallel plate type of α-Widmanstatten structure. The microstructure which is composed of relatively short plates in a random distribution which interweave each other within the prior-β grains is known as a basketweave structure. The prior-β grain boundaries are a preferred nucleation site for long plates which are parallel with each other. This type of structure is called parallel plate. The major factors influencing the formation of two different types of α-Widmanstatten structure are impurity content and cooling rate. The impurities (or second-phase particles) in Zircaloy-4 had variously been identified as zirconium carbide (3), zirconium phosphide (4), Zr-Fe-Cr compounds (5), and elemental silicon (6). The existence of these second-phase particles is well agreed upon, as is the fact that an abundance of these particles promotes the basketweave structure. However the relative effects of the different impurity elements on β→α-Widmanstatten transformation is not well documented and is open to some disagreement.
In order to better understand the influence of these second-phase particles and cooling rate on the microstructural features of the α-Widmanstatten structure, the present study was initiated. The impurities of concern here are carbon, phosphorus and silicon. The cooling rates were varied from furnace cooling (~0.01°C/s) to a dry ice-acetone quench (~7000°C/s). Ten batches of commercial tubing containing a wide range of C+Si+P phosphorus contents was obtained for this study. All batches of tubing were within the chemical specification for nuclear fuel cladding. In order to better examine the effect of phosphorus alone on the microstructural features, a range of Zircaloy-4 was made containing up to 160 ppm phosphorus. The C+Si+N+O content of these melts was kept as constant as possible. This part of the study had particular importance with respect to CANDU-PHW fuel cladding since although the evidence is that the P content can affect the microstructure in the brazed zone, there is no P content given in the specifications for the Zircaloy-4 fuel cladding.

The desirable microstructure features in the braze effected zone of Zircaloy-4 are a basketweave-type microstructure and a small prior-β grain size. The maximum size of the prior-β grains as specified by AECL (Atomic Energy of Canada Limited) is 130μm, or less than three grains through the wall thickness of the cladding. For larger grain sizes the tubing rejected because of insufficient strength. Therefore, there is a need to consider effect of brazing cycle on
prior-β grain size. The parallel-plate type of structure can itself produce an easy crack path, through the wall of the tubing. This is particularly true when there is stress corrosion cracking in presence of fission product iodine. Thus the need for a small prior-β grain size plus basketweave-type microstructure.
CHAPTER 2

Literature Review

2.1 The Allotropic Transformation

Zirconium has two allotropic modifications, the hcp (α) structure with a c/a ratio of 1.593 is stable from room temperature to 863°C and the bcc (β) structure is stable from 863°C to 1860°C, the melting point (7). Burgers (8) was the first to study the crystallography of the β→α transformation in Zr. He used rods of iodide-refined zirconium single crystals with the lengths of these rods parallel to either the [111] direction or the [001] direction. The side-faces of both rods were parallel to the {110} planes. Burgers proposed the crystallographic relationship between the α and β phases was (0001)α//(110)β and [11̅20]α//[11̅1]β, and the mechanism of the transformation was shear. Both the crystallographic relationships and transformation mode are still the subject of debate. In their review paper, Northwood and Lim (7) conclude that one of three mechanisms could be operating in the β→α transformation, namely: (1) thermally activated nucleation and growth with long range diffusion; (2) diffusionless shear (martensitic); and (3) massive. Almost all of the crystallographic transformation studies in zirconium involved heating the Zr crystal bar above 863°C, maintaining it in the β phase and then subsequently cooling to the α phase region. Gaunt and Christian (9) heated their specimens to 1150°C for 36h and then quenched them in brine. They found that the (001) plane of β structure was parallel to (0001) plane of α structure and the habit plane was
\{0.468, 0.488, 0.737\}_B$, not the traditional Burgers orientation, (\overline{4}33). With respect to transformation mechanism, it has been found to be dependent on the orientation of the original hcp crystals from which they were formed during any previous $\alpha \rightarrow \beta$ transformation. According to Akhtar (10), if the zirconium crystal was crystallized from the melt, then the $\beta \rightarrow \alpha$ transformation mechanism was of the massive type. However, the transformation would be of the shear type if the matrix of $\beta$ phase was produced by a prior $\alpha \rightarrow \beta$ transformation.

Ostberg (11) suggests that the allotropic transformation from hcp to bcc in the Zircalloys (Zr-Sn alloys) is of the eutectoid rather than the peritectoid type and a typical Zr-Sn-Fe or Zr-Cr-O system is a standard reference Zircaloy system. In these systems, the eutectoid valley of the beta stabilizing binary extends upwards parallel to the $(\alpha+\beta)$ to $\beta$ transus of the alpha stabilizing binary. In zirconium, tin and oxygen are alpha stabilizers while chromium and iron produce eutectoid type transformations. Ostberg also suggests that although some strain is involved in the $\alpha \rightarrow \beta+\alpha$ transformation of Zircalloys at high temperatures, the transformation itself is not a pure shear transformation.

There is a considerable body of literature on phase transformations in the Zircalloys, because of its relationship to safety problems in a nuclear reactor. LOCA (Loss of Coolant Accident) is one of the main safety concerns of
the nuclear industry. The cladding's crystallographic structure would be significantly changed during LOCA. In order to better understand the transformation mechanism in Zircaloys, Corchia and Righini (12) looked at the kinetic aspects of the phase transformations in Zircaloy-2 using electrical resistivity and metallographic techniques on specimens of various thermomechanical histories (as-received, annealed, annealed and quenched). Generally, the specimens that were previously heated into the $\beta$ phase underwent the phase transformation over a wider temperature range and a greater part of their resistivity change took place at higher temperatures (by 20-30K) than for the as-received specimens. Microscopically, the as-received specimens had equiaxed grains of an average diameter of several microns. The intermetallic phase $\text{x}$ (exists between the overlapping zone: $\alpha+\beta$ between 1150 and 1250K; $\alpha+\beta+x$ between 1080 and 1150K; $\alpha+x$ between 770 and 1080K) precipitates should have been present in noticeable quantities but they were not resolved by the optical microscope. For the annealed specimens, the $\alpha$-grains were present as parallel lamellae inside the former $\beta$ grain, while the $\text{x}$ intermetallic compound precipitated in a large quantity at the $\alpha$-grain boundaries. The quenched specimens were composed of a plate-like structure with randomly dispersed acicular grains of small dimensions, and the $\text{x}$-phase is absent because of the high quenching rate. They (12) concluded that specimens with different initial microstructures passed through the phase transformation with different kinetics and the $\text{x}$
secondary precipitate is one of the most important factors controlling the kinetics of the phase transformation. Grain size can also affect the kinetics of the phase transformations. The α-grain boundaries can act as β phase nucleation sites during the transformation. As a result, the coarse-grained material would have a higher transformation temperature and the transformation characteristics are similar to the quenched specimens, when the specimens possess a fine-grained structure.

2.2 The Influence of the Impurity Content on the Microstructural Features of Zircaloy-4

Second-phase particles (i.e., high impurity contents) in Zircaloy-4 can play a major role in promoting the basket-weave structure. As mentioned before which particular impurity element(s) does affect the α-Widmanstatten structure after the β→α transformation is still the subject of much debate.

Zirconium carbide particles were found using both electron and x-ray diffraction by Swedish workers (3). ZrC had a face centered cubic structure with a lattice parameter of approximately 4.7 Å. These particles were believed to be reprecipitated after the brazing process (i.e., cooling). The shape of the particles was irregular when looked at using a high magnification. The particles were located at the center of a group of divergent plates when the carbon content of the Zircaloy-4 fuel cladding was over 100 ppm. No carbide particles were found between the interweaving plates
if the carbon content was below 50 ppm. It is well recognized that second-phase particles are the main factor for promoting \( \alpha \)-Widmanstatten basketweave structure in Zircaloy-4, because they act as nucleation sites on a common habit plane in and along prior-\( \beta \) grain boundaries. The second-phase particles (or impurity elements) which had been identified are zirconium carbide (3), zirconium phosphide with a lattice parameter of 5.25\( \text{Å} \) and a NaCl cubic structure (4), Zr-Fe-Cr compounds (5), Zr\(_{0.22}\)C\(_{0.38}\) with a lattice parameter of 4.633\( \text{Å} \) (13), elemental silicon with a lattice parameter of 5.430\( \text{Å} \) (6) and oxygen (14). These second-phase particles or impurity elements play an important role in either controlling the transformation and microstructure developed or in giving anisotropic mechanical properties to the Zircaloy-4 fuel cladding. The controversial point is which of these second-phase particles are the nucleating sites for promoting \( \alpha \)-Widmanstatten basketweave structure. Okvist and Kallstrom (3) found that the impurity elements such as oxygen, tin, iron and chromium did not affect the \( \alpha \)-Widmanstatten structure but carbon did have an effect and that a basketweave structure would only be formed when the carbon content ranged between 100 ppm to 200 ppm. At lower carbon contents, a parallel plate structure was formed. At the same time, Holt (4) suggested that an abundance of randomly distributed second-phase particles or impurities present in the prior-\( \beta \) grains was the key for forming basketweave structure after the \( \beta \rightarrow \alpha \) transformation. He suggested that the
nucleation sites might be related to the carbon, oxygen, nitrogen and phosphorus impurity elements. Holt also suggested that the difference in α-Widmanstatten morphologies in Zircaloy-4 was coincident with a change in the kinetics of the beta to alpha phase transformation. The change in kinetics was considered to be due to a difference in nucleation mechanism rather than a difference in growth mechanism. Woo and Tangri (14) in their work on the effects of oxygen content and cooling rate on the microstructure of β-quenched Zircaloy-4-Oxygen alloys, concluded that increasing oxygen content led to a reduction in the martensitic content, and promoted parallel plate formation at a cooling rate of about 90°C per second. Most recently, work by Fong and Northwood (15,16) indicated that carbon, silicon and phosphorus can play a role in the nucleation of the basketweave structure. The higher the impurity (Si+C+P) content, the smaller the prior β grain size and the greater the tendency to form a basketweave structure.

The zirconium carbide particles are, as mentioned before, irregular in size, and due to their small size can only be revealed at high magnifications. According to Okvist and Kallstrom (3), the complex particle shape could result from eutectic solidification of small volumes of the last remaining melt, as can be predicted from zirconium-carbon phase diagram. Fong and Northwood (6) who identified the shape of second-phase particles in Zircaloy-4 nuclear fuel sheathing by bright-field image TEM methods showed that
zirconium carbide had a "banana-shaped" form, whereas Si had an angular morphology and phosphorus containing particles had a spongelike morphology. Using both the electron spectroscopic image and the electron energy loss spectroscopy technique (EELS) they found that the phosphorus-containing second-phase particles were fairly numerous in batches of cladding forming the basketweave α-Widmanstatten structure. Most recently, the morphology (shape, size, distribution, etc.) and composition of intermetallic second-phase particles in Zircaloy-2 (similar to Zircaloy-4 with a nickel addition) has been studied in detail by Chemelle et al (17).

Prior to this work, the intermetallic second phase particles in Zircaloy-4 had been investigated by a number of workers (3,4,5,6) and it was found that the Zr-Fe intermetallic phase could be seen only after a suitable heat treatment (18). The intermetallic second phase particles in Zircaloy-2 always appeared in the form of a compound which was composed of three different elements (Fe, Cr, Ni). Chemelle et al found that either a nickel-bearing or a chromium-bearing, and some particles containing both of these type, plus a nickel-bearing particle would precipitate first and this was followed by a chromium-bearing particle. The nickel-bearing particle was tetragonal with lattice parameters of a = 6.5Å and c = 5.3Å and the chromium-bearing particle was hexagonal with a = 5.1Å and c = 8.3Å. \( \text{Zr}_2\text{Ni}_{0.4}\text{Fe}_{0.6} \) and \( \text{ZrCr}_{1.1}\text{Fe}_{0.9} \) are typical second-phase particles of the nickel-bearing and the chromium-bearing type particles in
Zircaloy-2, respectively. The size of the second phase particles varied from 0.2-1.0µm and most of the particles were spherical or rectangular in shape but ovoid or angular particles were sometimes present. There were no zirconium-iron particles and no particles containing both nickel and chromium. Tin was found in solid solution in the matrix, but not in any particles. The morphology of second-phase particles were investigated by TEM with extraction replicas and STEM was used to analyze the particles composition. As previously noted in the work by Corchia and Righini (12), these intermetallic compounds have a strong effect on the kinetics of the phase transformation but a more limited effect on the temperature range of transformation. Recently, the presence of impurities has been shown to prove to be very important in the first steps of the phase transformation in zirconium (19).

These second-phase particles cannot only be recognized and identified by electron and x-ray diffraction or EELS, but also can be revealed by a suitable optical metallographic technique. Such a technique was developed 10 years ago by Kaufmann et al (20), who applied it to the evaluation of low solubility compounds by the so-called 'Anodizing' method. This method is based on the fact that the different intermetallic compounds have different colour contrast after anodizing. The thickness of the anodized film is dependent only on the chemical composition of the material being anodized and the grain orientation. The different film
thicknesses result in different interference colours which can then be evaluated with an optical microscope. Different phases and intermetallic compounds show colour differences which aids in their observation and identification. The method is easy to use but tedious and the results sometimes can be confused due to staining. In order to investigate the size, shape and distribution of intermetallic compounds such as carbides, phosphides and silicides of zirconium alloys, the following procedure is recommended by Wah Chüng metallographers (20). The metallographic sample is first polished on successively finer grit abrasive paper down to a 3/0 grit and then polished on a wheel rotating at approximately 1000 rpm using an abrasive solution (2 to 5 grams of 0.3μm alumina diluted with 150 ml of water), plus a chemical polishing solution (250 ml H₂O: 22 ml HNO₃: 3 ml HF). The wheel polishing at approximately 1000 rpm is continued for several seconds to allow an even film to form on the nylon cloth, then the speed is reduced to approximately 550 rpm and moderate pressure is applied between the wheel and the sample. When the sample is removed from the wheel, it is washed immediately with cold water. To anodize the sample surface, the solution (60 ml absolute ethanol, 35 ml water, 20 ml glycerine, 10 ml lactic acid (85 percent), 5 ml phosphoric acid (85 percent) and 2 g citric acid) is kept in a stainless steel beaker, and a D.C. voltage was applied between the sample surface and the stainless steel beaker. The negative lead of the voltage source is attached to the
beaker and the positive lead to a probe (a point tungsten wire 0.1 in. diameter by 2½ in. long) which is contacted to the sample surface. The probe is held on the sample surface until the current (200V, 1A) decreased to zero and the sample shows an even colour over the whole surface. As a result, the matrix colour varied from grain to grain due to the difference in preferred orientation between grains. At 115 V a deep gold colour is exhibited by silicides and phosphides compared to a yellow colour for the carbides. Phosphides anodized at 115 V were a bright gold colour, and had a shiny, mirror-like surface. It was interesting when the phosphide was looked at under a higher magnification, and it was seen to be a very sharp, pointed, intermetallic with very little rounding. The angularity and sharpness of these intermetallic compounds was altered little by heat treatment at 1204°C for 24 h.

2.3 The Influence of Cooling Rate on the Microstructural Features of Zircaloy-4

In Zircaloy-4, cooling rate is another important factor influencing the microstructural features. Since the tendency to form α-parallel plate structure and large grain size is primarily dependent on temperature/time considerations, it would be worthwhile to review the joining processes used in the production of fuel bundles from a temperature/time standpoint.

There are two processes commonly used to join the Zircaloy end plate to the fuel elements; these are tungsten
inert gas (TIG)-arc welding and resistance welding processes. Resistance welding gives a more rapid rate of heating and cooling than TIG welding; its cooling rate being $\sim 10^3 \, ^\circ C \, sec^{-1}$ or at least 10 times faster than TIG welding ($10$ to $10^2 \, ^\circ C \, sec^{-1}$) (21, 22). Another excellent feature of resistance welding is that it can be performed under any gas pressure, or even in air, and the HAZ (heat affected zone) is very small because of short process time. Bardoni and Olmedo (21) conclude that the resistance welding process, due to the rapid welding cycle, has the following advantages over TIG welding:

1. smaller HAZ size;
2. smaller grain size;
3. less contamination by impurities;
4. more homogeneous distribution of second phase particles.

Using a TIG welding process, the weld seam has a columnar $\beta$-grain indicative of fusion and acicular $\alpha$-needles. The HAZ possesses an intermediate grain size between that of the weld seam and the base material. The welding zone can be characterized by its microstructure; at the fusion zone (cooling rate of $2-10^0 \, ^\circ C \, sec^{-1}$) the microstructure is coarse $\delta$ (Widmanstatten parallel plate). The microstructure changes $\delta \rightarrow \alpha + \beta$ ($\alpha$-Widmanstatten basketweave) $\rightarrow \beta$ (with fine plates), when the cooling rate is changed from 10 to $10^3 \, ^\circ C \, sec^{-1}$ along the tube. The $\alpha$ phase recrystallizes and small polygonal grains are obtained in the remote heat-affected zone. The structural changes from the fusion
zone to the top of the end cap are \( W_{\beta \alpha} \rightarrow W_{\beta \alpha} + W_{\beta} \rightarrow W_{\beta} \) (21,23). According to Woo and Tangri's (14) work, the microstructure changes in the order: lenticular \( \alpha \rightarrow \) parallel plate \( \alpha \rightarrow \) basketweave \( \alpha \rightarrow \) martensitic \( \alpha' \) with increasing cooling rate. This change in microstructure is very closely related to the change in mechanical properties (24). At a cooling rate of approximately \( 90^\circ C/s \), increasing oxygen concentration in Zircaloy-4 promotes the formation of a parallel plate structure with large plate width (14). An increasing cooling rate would give a smaller plate width, because the oxygen has less time to diffuse from the beta to the alpha grains and the rapid nucleation of new plates predominate over growth of existing plates. Also, the faster the cooling rate, the more nucleation sites are created by oxygen within the \( \beta \) grains which would favour the formation of a basketweave structure. Twinning can be seen in low oxygen (0.13wt\%) content alloys only if the cooling rate is fast enough (\( >2000^\circ C/s \)) to depress the \( M_S \) temperature to a low enough temperature. Woo and Tangri (14) also showed that the plate width in an Zircaloy-4 oxygen-containing alloy decreases significantly when the amount of undercooling (\( \Delta T \)) increases or cooling rate increases. The relationship between undercooling and plate width is given by \( W \propto (\Delta T)^{-1.27} \). This relationship is similar to that found by Chadwick (25) for interlamellar spacing and plate width in a eutectic alloy solidification.

Welding and brazing processes used to assemble the
fuel bundle have to be controlled to minimize excessive grain growth, because the brazed zone microstructure is affected both by the impurity content and the brazed conditions (time/temperature). At severe brazing condition, i.e., higher temperature and a longer time, the grain size (320±95μm, at 5m/1100°C, WQ) almost two times larger than at less severe conditions (125±15μm, at 1m/1050°C WQ) (15). Therefore the most suitable brazing process uses shorter brazing times and lower brazing temperatures. The brazing metal is Zr-5wt%Be (26) with a melting point of 965°C, which was selected for CANDU-PHW reactor fuel cladding mainly because of its good wetting properties and high mechanical strength and low neutron absorption cross-section.

The increased prior-β grain size produced by decreasing the cooling rate is of concern in SCC (stress corrosion cracking) of fuel cladding by fission products such as iodine and tellurium. SCC of Zircaloy by iodine vapour was reported by Rosenbaum et al (27,28) and was found to be due to iodine concentration at the fuel/pellet interface. The unique feature indicating the occurrence of SCC in Zircaloy is flat cleavage planes and the crack propagation can be either both intergranular and/or transgranular as a consequence of SCC. As mentioned before, the propagation of cracks during SCC is retarded by having a large number of randomly oriented α-plates, interweaving each other (as from the brazing operation) plus a small grain size.
In summary in order to achieve better mechanical properties and corrosion resistance of commercial Zircaloy-4 fuel cladding at braze heat-affected zone, one must increase the percentage of basketweave-type structure and in general make the structure finer. The basketweave structure which consists of many randomly oriented α-plates has a smaller effective grain size than the parallel plate structure thus resulting in better mechanical properties. The basketweave-type microstructure, which is the most desirable structure in braze heat-affected zone, is more readily produced by increasing either the impurity content or cooling rate (3,4,6,14,15,16).

2.4 The Mechanism of Formation of an α-Widmanstatten Basketweave Structure

The formation of either a 'basketweave-type' microstructure or 'parallel-plate type' of α-Widmanstatten structure had been described by several authors (3,4). It has been found that if the impurity content in Zircaloy-4 is high and there is an abundant and random distribution of second-phase particles in numerous habit planes in the prior-β grains, then the α-Widmanstatten structure formed on cooling from the β to α phase would have a basketweave structure. There would be a parallel plate structure if the prior-β grain boundaries are the nucleation sites for these plates and not the second phase particles. There are very few if any, theoretical descriptions in the literature regarding the formation of a basketweave-type Widmanstatten
structure in Zircaloy-4.

Looking at the nucleus which acts as a nucleation site of the plate, from a thermodynamic standpoint, Holt (4) derived an equation for the formation of a critical nucleus. This equation relates the Gibb's free energy and surface energy as follows:

$$\Delta G_{\text{act}} = \frac{4}{27}(\pi/k^2)(\gamma_1^3/\Delta G_v^2)$$  \(1\)

where,
- $\Delta G_{\text{act}}$ = Gibb's free energy;
- $k$ = the thickness of a flat disc;
- $\gamma_1$ = energy of coherent $\alpha+\beta$ interface;
- $\Delta G_v$ = volume free energy change from $\beta$ to $\alpha$.

Under the circumstances where the volume of the phase does not change and its thickness is kept constant, then:

$$\Delta G_{\text{act}} = C\gamma_1^3$$  \(2\)

According to Chadwick (25), the degree of undercooling is the summation of a series of undercooling terms, that is:

$$\Delta T = \Delta T_C + \Delta T_r + \Delta T_k$$  \(3\)

where,
- $\Delta T_C$ = a constitutional undercooling due to the enrichment of the liquid by solute;
- $\Delta T_r$ = an undercooling due to the curvature of the solid surface in contact with the liquid;
- $\Delta T_k$ = an undercooling required by the kinetic process of solidification.
In the present case, the transformation is solid to solid, and therefore equation (1) should include a strain energy term as follows (29):

\[ \Delta G_{\text{act}} = \frac{k \gamma^3}{(\Delta G^v + \Delta G^s)^2} \]

However, it can be shown (30) that:

\[ \Delta G^v \approx -(\Delta S^v)(\Delta T) \]

where \( \Delta S^v \) is the volume entropy change for the transformation and \( \Delta T \) is the undercooling,

\[ \Delta G_{\text{act}} = \frac{k \gamma^3}{(\Delta S^v)(\Delta T + \Delta G^s)^2} \]

From kinetic theory, it can be shown that the rate of nucleation \( \dot{N} \) is proportional to the number of critical-sized embryos present, i.e.,

\[ \dot{N} \propto \exp[-k \Delta G_{\text{act}}/RT] \]

\[ \dot{N} \propto \exp[-\frac{k' \gamma^3}{(\Delta S^v \Delta T + \Delta G^s)^2}/RT] \]

where,

\[ k \neq k' \neq k'' = \text{constant} \]

Thus, when \( \Delta T \) increases (as it will with an increase in cooling rate), the nucleation rate \( \dot{N} \) will increase exponentially within \( \sim (\Delta T)^2 \). The nucleation rate and refinement of structure is extremely sensitive to cooling rate.
2.5 Quantitative Metallography

Quantitative metallography is used to determine the volume fraction of morphologies (e.g., grain counts, grain sizes and distributions) and dimensions of the structure (e.g., plate width and length) constituents.

The commonly used technique for volume fraction analysis (31) are:

(a) an areal analysis
(b) a lineal analysis
(c) a point count analysis

In an areal analysis, measurement with a planimeter (or other means) of the area of a constituent intercepted by the polish plane. For a lineal analysis, a measurement of the fractional line length intercepted. It is usually performed by traversing the specimen under the cross hairs of a microscope and recording the distance travelled in each constituent.

For a point-count analysis, the fractional number of randomly or regularly dispersed points falling within the boundaries of a two-dimensional feature on a plane, or within the boundaries of a three-dimensional feature in a volume, provides an unbiased estimate of, respectively an areal or volume fraction of that feature.

The above methods require at least one and generally several sampling stages. Apart from any experimental errors, there will always be a statistical uncertainty associated with the final results, and the statistical analysis for the above techniques has been developed by Hilliard and Cahn
The method generally used for determining the size of grains or constituents in structures (e.g., lamellae in eutectic structures) is the linear intercept technique. The obvious difficulty with this method is the uncertainty in the measurements resulting from the fact that a polish plane is only a two-dimensional representation, while the grain or lamella plate is a three-dimensional object. For example, in measuring the lamella spacing in pearlite, unless the polish plane is virtually perpendicular to the lamella interfaces, the interlamellar spacing will always measure larger than the true spacing. A considerable statistical formalism has been developed by Fullman (32) to reduce the data obtained from arbitrarily located polish plane to give the mean grain size or lamella spacing (mean minimum value).
CHAPTER 3

Experimental Methods

3.1 Zr-P Alloy

High phosphorus content Zircaloy-4 ingot supplied by Teledyne Wah Chang, Albany, Oregon, was used as the base material. The manufacturers' analysis for the major impurities was as follows: C 70-80 ppm, Si < 20 ppm, and P 160 ppm. This high phosphorus content Zircaloy-4 was mixed with a low carbon Zircaloy-4 containing < 20 ppm P to make the series of alloys with varying phosphorus content from 42 to 160 ppm.

Before melting, 50 grams for charges were made up by mixing the required amounts of the two phosphorus-containing Zircaloy-4 ingots. In calculating the required amounts, an allowance was made for phosphorus loss during the vacuum arc melting. The surfaces of the metal pieces for the melt were cleaned by grinding and then dried by acetone. In order to eliminate the effects of other impurities (especially oxygen) strict procedures were followed in the melting process. The high vacuum arc-melting furnace with copper crucible was supplied by Westinghouse Canada Limited, and is shown in Figure 2. The pre-melt procedures are as follows:

1. Make sure copper crucible is cooled. The melting point of Zircaloy-4 is over 1800°C. At such high temperatures, the copper crucible must be cooled by cold water flowing around it. The cold flowing water not only keeps the crucible from going out of shape, but also guarantees that no copper can contaminate the product since
the molten Zircaloy-4-P alloy freezes as it contacts the crucible and shrinks away from the walls before it has time to alloy with the copper (32).

(2) Clean the crucible with acetone. If necessary, it should also be cleaned with sulfuric acid (10H₂SO₄:90H₂O by volume). Dry the crucible by hot air. This procedure is taken to keep any contaminants as low as possible.

(3) Make sure the quartz capsule is clean. Its function is to keep the melting process under high vacuum.

(4) Start the vacuum pump. As soon as the mixed alloy is placed in the crucible, the system is set up as indicated in Figure 2.

(5) Pump the whole system down to -30 psi for approx. 15 minutes.

(6) Increase the pressure up to 100 psi using commercial purity argon to maintain the pressure.

(7) Connect the negative current to the arc-electrode and make sure it is tight. If it is not tight, the production arc wavers and is difficult to control during the melting process.

(8) In order to keep the melting processes as short as possible, the working current is maintained at 150 amp. Melting time is usually 3 minutes. The arc-electrode is controlled by hand and produces an arc only when the electrode slightly touches the metal. Zircaloy-4 is very good getter for residual gases at elevated temperatures. Therefore, after melting, the ingot should be kept in the
vacuum capsule until it is cooled. The ingot is taken out and cut into two or three pieces, then remelted again. The re-melt procedure is done three or four times to guarantee the homogeneity of the alloys.

3.2 Heat Treatment

The aim of heat treatment was to simulate the brazing conditions encountered in the attachment of appendages to Zircaloy-4 fuel-cladding. As mentioned elsewhere (1) in the literature, the brazing cycles are approximately 1 minute long at temperatures in excess of 1000°C. Our simulations involved extremely demanding temperature cycles with times of 5 minutes at 1100°C. This is a good test of the fuel cladding since if a fine grain size material having a basketweave structure can be formed under these conditions then an acceptable product will most certainly be formed during commercial induction brazing cycles.

There were ten different batches of Zircaloy-4 fuel-cladding of 0.4 mm wall thickness and 15 mm diameter. They were sectioned into 20 mm lengths for heat treatment. Totally, there were sixty material/cooling rate conditions for the experiment (in six different cooling rates, 10 different materials). The major impurity contents of ten different batches of Zircaloy-4 are listed in Table 1. The cooling rates were: furnace cooling, air cooling, oil cooling, water quench, brine quench, and dry ice-acetone quench, going from the low cooling rates to extremely fast cooling rates. The ingots of Zircaloy-4-P were also cut into sec-
tions 2 cm long and ground to remove surface contamination. Both of these specimens (Zircaloy-4 fuel-cladding and Zircaloy-4-P) were cut using a low-speed diamond saw. After cutting, both of these specimens were encapsulated in evacuated quartz capsules at a pressure of approximately \(5 \times 10^{-5}\) torr. The Zircaloy-4 commercial fuel-cladding in quartz capsules were heat treated at 1100\(^\circ\)C for 5 minutes, then each capsule was cooled in one of the cooling media as described above. Each capsule contained ten samples with the differing amount of the impurity contents. The Zircaloy-4-P specimens were heat treated at 1100\(^\circ\)C for 15 minutes for homogenization and formation of the \(\beta\)-phase and then air cooled to form the \(\alpha\)-phase. Such a treatment would simulate the braze treatment except that the time at 1100\(^\circ\)C was much longer than that used in practice. This was however required to fully homogenize the as-cast structure (in the case of Zircaloy-4-P).

3.3 Metallographic Preparation

The heat treated specimens were mounted in cold resin. After wet polishing with silicon carbide papers down to 600 grit, the commercial Zircaloy-4 fuel cladding specimens were swab etched/polished using a solution of 40 parts \(\text{HNO}_3\), 20 parts \(\text{HF}\) and 40 parts \(\text{H}_2\text{O}\). The etching solution of Zircaloy-4-P was 40 parts \(\text{HNO}_3\), 10 parts \(\text{HF}\), 10 parts \(\text{H}_2\text{SO}_4\), and 40 parts \(\text{H}_2\text{O}\). The time of chemical etching/polishing was not more than 1 minute. The specimens were dried completely and kept in a desiccator to await metallographic examination.
3.4 Metallograph and Ancillary Equipment

Apart from the high vacuum arc furnace described in section 3.1, the main experimental facility used in this study was a Leitz optical microscope with bright field illumination and camera attachment. The advantages of this optical microscope is that it possesses a large enough image screen for manual counting and a series of high magnification lenses. The microstructural features which were quantitative analysed were: the type of microstructure; prior-\(\beta\) grain size, plate width and plate length. An ASTM standard counting grid with 187 intersection points was used to count the volume fraction of the type of microstructure in the \(\alpha\)-phase of the Zircaloy-4. A ruler with millimetre divisions was used to measure the grain size, plate width, plate length.

3.5 Quantitative Metallography

In order to investigate the effect of (C+P+Si) content and cooling rate on the microstructural features of Zircaloy-4, the following observations were made: the type of \(\alpha\)-Widmanstatten structure; grain size; plate width and plate length.

3.5.1 Type of Microstructure

In general, there are two types of microstructure - these being the parallel-plate structure and basketweave structure. For a more quantitative description of the microstructure in Zircaloy-4 after the \(\beta\rightarrow\alpha\) transformation, the microstructures were divided into five types, namely, tendency to parallel plate structure (Tp), parallel plate
structure (Pa), tendency to basket weave structure (Tb),
basket weave structure (B) and martensitic structure (M). The
micrographs illustrating these structures in the Zircaloy-4
and high phosphorus Zircaloy-4 are shown in Figure 3(a), (b),
(c), (d), (e), and Figure 4(a), (b), (c), (d), respectively.

In this particular study, for determining the relative
fractions of various structures (B, Tb, Tp, Pa), a transparency
with a 187 intersection-point counting grid was superimposed
on the bright field image on the metallograph screen and 30
to 40 areas were counted per specimen. The procedure is
then to count the number of intersection points that lie at
the microstructure of interest. To calculate the volume
fraction of one of the microstructures of interest, the number
of points the microstructure occupied was divided by the
total intersection points on the counting grid. Usually the
volume fraction of the microstructure of interest was obtained
only after repeated counts of at least three times for any
sample representative of particular impurity content/cooling
rate. The magnification which was used to count the volume
fraction of the microstructure was 320 times for the Zircaloy-4
samples and 80 times for the high phosphorus-containing sam-

In this investigation, no attempt is made to determine
the true mean dimensions of the grains and plates (plate
width or plate length), and therefore the statistical treatment
to give such results is omitted. The complexities of the
structures, i.e., the basket weave and tendency to basket weave
morphology, do not lead themselves to rigorous statistical
treatment except for very large sample and count numbers.
For the purpose of this investigation, in determining the effects of impurity levels and cooling rates on structure fineness, the "apparent" grain sizes and plate dimensions are used, that is the average sizes and dimensions obtained from the direct measurements, without the statistical analysis (other than averaging).
3.5.2 Grain Size

For Zircaloy-4 samples, up to 100 grains were counted at 80 times magnification and at least 30 grains were counted in the high phosphorus-containing Zircaloy-4 at 32 times magnification. The grain sizes were measured using a centimetre rule in both the transverse and longitudinal directions of the tubing. The grain size is calculated by taking total distance traversed and dividing it by the number of grains contained in that distance. The grain size counting method can be simplified by the following mathematical expression:

$$\text{GS(\mu m)} = \frac{\sum_{i=1}^{N} (x_i + y_i)}{2N} \cdot \frac{1}{M}$$

where, $x_i$ = horizontal dimension of the $i^{th}$ grain in $\mu m$;
$y_i$ = vertical dimension of the $i^{th}$ grain in $\mu m$;
$M$ = magnification of the optical lens;
$N$ = the total number of grains which are measured for one sample.

3.5.3 Plate Width and Plate Length

The plate width and lengths were measured using a scale and up to 40 spacings in one sample were measured. The decision on how many readings should be taken in one area was dependent on the distribution and number of the plates in that area. The magnification was varied with the thermal treatment that had been applied to the sample. A high magnification was used if the sample had been cooled at a rapid cooling rate. The optical lenses were varied from 32 times magnification to 1000 times magnification.
The 800x to 1000x optical lenses were used for counting when the cooling rates were water quench, brine quench and dry ice-acetone quench.

3.6 SAS Analysis

The SAS (34) (Statistics Analysis System) computer program was used to fit empirical equations to relate the impurity content/cooling rate to the quantitative microstructural information. SAS uses a logical language specifically developed for the purpose. The GLM (General Linear Model) procedure provided for multiple regression analysis was used for this particular investigation, in which the input data was volume fraction structure, grain size, plate dimensions, impurity levels, and cooling rate.

3.7 Photomicrography

All micrographs were taken on the camera attached to Leitz optical microscope. The OM lenses magnification was 100x, 200x or 500x and bright field illumination was used.
CHAPTER 4

Results

For convenience, the results were summarized into two separate sections, one dealing with the high phosphorus content (Zircaloy-4-P), and the other with the commercial Zircaloy-4 fuel cladding. SAS empirical equations are presented in each section. In addition to the empirical equations, the relationships between the quantitative results describing the microstructural features (% of type of microstructure, grain size in \( \mu m \), plate width in \( \mu m \), plate length in \( \mu m \)) and the impurity content/cooling rate are presented in the form of tables, figures and micrographs.

4.1 The High Phosphorus Content Zircaloy-4

There is a concern that segregation of phosphorus existed even after the 1100\(^\circ\)C heat treatment for 15 minutes. However from an inspection of micrographs given in Figure 5 for the alloy containing 160 ppm phosphorus, it can be clearly seen that the needle-like structure in the as-cast material (Figure 5(a)) is largely eliminated and the distribution of the microstructure becomes more uniform, Figure 5(b), after the homogenization treatment.

The quantitative analysis of the morphologies (% of tendency to parallel plate structure, % of parallel plate structure, % of tendency to basketweave structure, % of basketweave structure, grain sizes in \( \mu m \) and plate width and length in \( \mu m \)) are summarized in Table 2 as a function of the phosphorus content of each sample. The micrographs representing the different types of microstructure are
shown in Figure 4 and a description of these microstructures is given in Table 3. The relationship between the microstructural features: (% of tendency to basketweave plus basketweave, grain size, plate width and plate length) and phosphorus content as analyzed by SAS and given in the form of empirical equations are summarized in Table 4. It should be noted that the carbon content in the low phosphorus samples was not analyzed. Although the carbon content is low, the procedure in preparing the ingots results in carbon content variation, and thus some contribution to structure refinement in the high phosphorus samples is due to the slight carbon variation. In general, for the same cooling rate the grain size of Zr-4-P alloy was finer and the percentage of the basketweave type microstructure was higher if the phosphorus content of the sample was high. The plate width and plate length also decreased with increasing phosphorus content. The computed values (computed using the empirical equations from SAS) and the measured values of (% basketweave structure plus % tendency to basketweave structure), grain size, plate width and plate length versus the phosphorus content are plotted in Figures 6, 7, 8, 9.

4.2 The Commercial Zircaloy-4 Fuel Cladding

4.2.1 The Influence of the Impurity Content on the Microstructural Features

The impurities of concern are C (carbon), P (phosphorus), and Si (silicon). Impurity analysis for each batch of tubing is listed in Table 1.
4.2.1.1 As-Received Condition

The grain size of as-manufactured Zircaloy-4 fuel cladding should not be greater than 30 μm and the grains should be equiaxed. The above requirement is met only if the Zircaloy-4 fuel cladding batch contains a high impurity (C+P+Si) content. This is illustrated in Figure 10(b) where the grain size was small and the grains equiaxed in the sample containing the highest impurity content (C+P+Si = 393 ppm) of the ten batches. Although this tubing had passed through many deformation processes, the grains appeared undeformed. This was probably due to the fact that the tubing had had a stress relief which produced recrystallization and a small grain size. On the other hand, the grain size of the batch with the lowest impurity content (C+P+Si = 151 ppm) had heavily deformed grains (Figure 10(a)) indicating that the tubing had experienced little or no recrystallization during the stress relief.

4.2.1.2 The Microstructure

The microstructure of the simulated brazed zone after the α→β→α transformation cycle was divided into five different types, namely, tendency to parallel plate structure (Tp), parallel plate structure (Pa), tendency to basketweave structure (Tb), basketweave structure (B) and martensitic structure (M), rather than the two general types, (Pa and B). The description of these structures is given in Table 3, and the representative microstructures of these five different types are shown in Figure 3(a), (b), (c), (d), (e), respec-
tively. The percentage of each type of microstructure for each impurity content/cooling rate combination is given in Table 5. Comparing Tables 1 and 5, it can be seen that the amount of martensite formed increases as the impurity (C+P+Si) content decreases. The size and shape of martensitic structure was also changed as the impurity content increased. The needle-like martensitic structure became finer and less needle-like severe as the total impurity content increased from 151 ppm to 231 ppm. The change in martensitic structure on increasing the impurity content is shown in Figure 11.

Closer inspection of Tables 1 and 5 shows that martensite is only formed in specimens A,B,F,I and J. These are the specimens whose carbon contents is 150 ppm or less. They are also the specimens with total (C+P+Si) of 235 ppm or less. The five specimens which did not form martensite had carbon contents of 170 ppm or more and had total impurity contents of 270 ppm or higher. Therefore, these tests could not distinguish the role played by the total impurity content compared with that of carbon acting alone with respect to the tendency to form martensite.

In general, the percentage of basketweave-type (i.e., B+Tb) structure was higher when the total impurity content was higher. Also, what parallel plate structure there was mostly of the 'tending to parallel plate' type rather than a true parallel plate (i.e., % Tp structure was higher than % Pa structure). Figure 12 illustrates the relationship between the total % of basketweave-type structure, (B+Tb) %, for air cooled Zircaloy-4 and the total impurity content. This plot indicates that (B+Tb)% would be 100% if the total
impurity content was over 320 ppm. Again, however the relative roles of the carbon content and the total impurity content are not separable from these tests. The two strongest basketweave forms (Specimens C and D) have the highest total impurity content (over 300 ppm) but also the highest carbon contents (over 240 ppm). The next three, in descending order of basketweave tendency are G and then E and H. These correspond to descending order for both total impurity content (298, 273, 270 ppm) and total carbon content (190, 180, 170 ppm).

In conclusion, it appears that tight restrictions on relatively low levels of P and Si contents are not necessary for commercial alloys.

With respect to the formation of a martensitic structure, less martensitic structure is formed if the impurity (C+P+Si) contents are greater than about 230 ppm then no martensite is formed regardless of cooling rate. The microstructural features of Zircaloy-4 are thus getting more desirable with increasing impurity (C+P+Si).
content since no martensite is formed and a totally basketweave type structure is formed.

4.2.1.3 Grain Size

The effect of the impurity (C+P+Si) content on the grain size of Zircaloy-4 fuel cladding is not so strong as it was on the type of microstructure. Table 6 summarizes the grain size measurements and correlates them with the impurity content and cooling rate. Generally, the grain size decreases with increasing the impurity content (Figure 13(b)). The elemental silicon is likely to play an important role as does C (carbon). Figure 13(a) is a plot of the effect of impurity content on the grain size for the air-cooled condition which may approximate the situation in actual production. Figure 14 is the case study of the sample containing 171 ppm C+P+Si. This sample was given a simulated braze at 1100°C for 5 minutes then subsequently air cooled. In this histogram, the (+) notation represents the grain size and the vertical direction is the number of the grains in this size. The circle (o) is representative of the average grain size in the interval. Totally, there are nine intervals and one hundred grains are counted. The intervals are [100,200],[201,300],[301,400],[401,500],[501,600],[601,700],[701,800],[801,900],[901,1000]. As can be seen in this figure, the highest frequency of the grain sizes which are concerned is in the [201,300] interval and the average grain size in this interval is 220μm. 66% of the grains are sized between 100μm and 400μm (100 < GS < 400). Also from this figure, 42% of the grain size are less than 300μm and
the average grain size in this interval (100<GS<300) is approximately 200\(\mu\)m. Statistically, the average grain in the 100<GS<400 size is approximately 250\(\mu\)m. This grain size is acceptable if the brazing temperature and time are considered. However, the impurity (C+P+Si) content of this sample is low (171 ppm) when compared with other batches.

4.2.1.4 PW and PL (Plate Width and Plate Length)

As expected, both the plate width and plate length (PW and PL) of Zircaloy-4 nuclear fuel cladding vary with the impurity (C+P+Si) content. Samples containing high impurity contents give a finer PW and shorter PL when compared with the low impurity content material; see Figure 15 and Figure 16. Tables 4 and 6 give the empirical equations (8,9) developed by SAS, and a summary of the experimental data for PW and PL, respectively.

Figure 17, which uses Equation (14) in Table 4 and only the air cooled data were inserted into the SAS package for analysis, gives no problem with fit. In other words, if only one set of data is used for analysis, then SAS gives a very representative empirical equation. There were a number of points which did not agree well with the computed values. The main reason is considered to be that most of the parallel-plate type microstructure is TP, and accurate data are difficult to get because of the small volume fractions. The approximating method is to measure all of the plates (if possible) which show up in one area, and then take twenty areas of different places of the sample into
account, rather than measure forty or fifty plates of the 
most representative plates in the different twenty areas.

The general equations, (6) (7), (8), (9) and (10) in 
Table 4 give a tendency of the relationship between the inde-
dependent variables (C,P, Si, Cr) and the dependent variables 
(B+Tb), F W(µm), PL(µm), GS(µm)) only. It cannot apply to 
an individual case, e.g., where cooling rate is constant. 
Equation (11), (12), (13), (14) give the grain size and 
plate dimensions as a function of impurity level for con-
stant cooling rate (air cooled - 100°C/sec.). It is evident 
in comparing the microstructures of Figure 20 that structure 
fineness is very sensitive to impurity levels, significantly 
increasing in fineness with increasing impurity content.

4.2.2 The Influence of Cooling Rate on the Microstruc-
tural Features

The cooling rates used in this study were: furnace 
cooling (~0.01°C/s), air cooling (~100°C/s), oil quench 
(~750°C/s), water quench (~5000°C/s), brine quench (~5700°C/s) 
and dry ice-acetone quench (~7000°C/s). The abbreviations 
Fur., Air, Oil, W, B, D are used for these cooling rates, 
respectively. The numeral cooling rates shown in brackets 
were calculated using the given wall thickness and the graph-
ical plots devised by Rumball using physical property data 
for dilute zirconium alloys (49).

4.2.2.1 The General Microstructural Features

In general, the percentage of basketweave-type struc-
ture and martensitic structure increases with cooling rate. 
This is because the fast cooling rate increases undercooling
(and hence nucleation rate) and also lowers the transformation temperature to below the \(M_s\) temperature. The influence of the cooling rates on type of microstructure is summarized in Table 5. Looking at this table, it should be noted that the martensitic structure is formed only in samples which are subjected to a fast cooling rate and which also contained a low impurity content \((C+P+Si<250 \text{ ppm})\) and a low C level \((<160 \text{ ppm})\). Cooling rates such as water cooling or faster promoted the martensitic formation, unless the impurity content was high \((>231 \text{ ppm } (C+P+Si))\). The empirical equations (6) and (7) in Table 4 derived by the SAS computer program, indicate that the cooling rate has an effect on the formation of B and B+Tb although the multiplying factor is small, 0.004 or 0.001 respectively. However, given the large variations in cooling rates (nearly 6 orders of magnitude) the net effect of a cooling rate change is quite marked. This is illustrated in Figure 21 for a sample containing 393 ppm \((C+P+Si)\). The structure is coarser if the cooling rate is lower and one is more likely to form a Tb structure than a B structure. Conversely, if the cooling rate was rapid, then the structure is fine and the plates interweaved with each other perfectly.

4.2.2.2 Grain Size

As can be seen in Table 6 and Figure 22, the grain size of the Zircaloy-4 did not change significantly on increasing the cooling rate, the slope of GS vs. cooling rate plot being very small. In fact, the grain sizes of Zircaloy-4 after the \(\beta\rightarrow\alpha\) transformation (Table 6) are quite large. In order to meet the specification requirements for
good service performance it is required that there be at least three grains across the wall thickness (0.4 mm) of Zr-4 fuel cladding, i.e., grain size not to exceed about 130 μm. Part of the requirement stems from the fact that the SCC from fission products is enhanced by a large grain size (35). From the histogram, Figure 14, of grain sizes in the sample with 171 ppm (C+P+Si) in the air cooled condition, most grains were in the 100 to 300 μm grain size interval. Thus, the grain sizes of Zr-4 in this experiment do not meet the requirements; however, the brazing time (5 minutes) in this experiment was exaggerated if compared with a practical brazing time (½ to 1 minute). Since time and temperature are the primary factors controlling prior-grain size (15,16) it should be fairly easy to meet the specification requirements.

4.2.2.3 Plate Width and Plate Length (PW & PL)

Figures 23, 24 illustrate the fact that both PW and PL are changed with a change in cooling rate, the microstructures coarsening with decreasing cooling rate. The influence of cooling rate on the microstructural features is summarized nicely in the series of micrographs in Figure 21.
CHAPTER 5

Discussion and Implications

Generally, the experimental results demonstrated well the fact that a high percentage of basketweave structure and a finer structure (smaller GS, PW, PL) could only be obtained in samples containing a high enough impurity content (either high in total (C+P+Si) content or individual (e.g., P) content.

As with the results section, this chapter will be divided into two main parts: Part one - Zircaloy-4-P alloy; Part two - Zircaloy-4 nuclear fuel cladding.

5.1 Zircaloy-4-P alloy

As is evident from all the results presented (Figures 6, 7, 8, 9), the microstructural features of braze zone of Zircaloy-4 fuel sheathing are significantly affected by the phosphorus content. In fact, no basketweave structure would form after the $\beta+\alpha$ transformation if the phosphorus content was zero. However, a small percentage of the basketweave structure is obtained in low phosphorus (5-20 ppm) content material, typical of commercial Zircaloy-4 fuel cladding. A completely 'basketweave-type' structure (i.e., including tendency to basketweave plus basketweave structure) can only be formed if the phosphorus content is as high as 200 ppm. From our experience in handling the high phosphorus content Zircaloy-4 melts, a high level (above 100 ppm) of phosphorus makes the sample very brittle and it cracks along the grain
boundaries after an $\alpha+\beta\rightarrow\alpha$ thermal treatment. This is in agreement with the literature on alloy steels (36) where the embrittlement is often due to phosphorus. If we compare the metal chips from machining the 42 ppm P and 160 ppm P alloys, Figure 25, it can be seen that the metal machining chips are broken into small pieces in the higher phosphorus content sample. According to author's experience with re-sulfurized free cutting steel, the metal chips such as for the 160 ppm P material in Figure 25 could not sustain any kind of mechanical forces. Therefore, it would be impractical to attempt to produce the basketweave structure by increasing the phosphorus content to such a high level. The fact that these phosphorus bearing particles act at nucleation sites for the basketweave structure can readily be seen in Figure 4(d) where a number of these particles can be seen "anchoring" the basketweave structure. With these particles nucleating the basketweave it would follow that the more particles then the greater would be the amount of 'basketweave-type' structure. Also if the basketweave structure nucleated at a greater number of sites then the structure would be expected to be finer. This is exactly what did happen with both the plate length and plate width decreasing as the phosphorus content is increased.

According to the empirical equations in Table 4, the phosphorus content does have an affect on GS, PW and PL, but not a very strong one. However, as already noted, the P content does have a strong effect on both the amounts of Tb
and B structure. The B structure could not form without some phosphorus being present, although a certain amount of (B and Tb) structure exists but this also depends on an increased phosphorus content to increase the amount of 'basketweave-type' microstructure, which is the most desirable structure in the braze zone of Zircaloy-4. More 'basketweave-type' microstructure with smaller PW and PL is formed with increased phosphorus content. As can be seen from Table 2, the percentage of Tp is higher than Pa. As is shown in Figure 4(a), it proved difficult to measure PW and PL accurately, which explains the difference between the measured and SAS's computed values. Usually, the PL of the structure is shorter than PL for the Pa structure as can be seen in Figures 3(a),(b),4(a),(b). As mentioned previously, there is no phosphorus content given in the specifications for Zircaloy-4 fuel cladding. However, as is evident from the data presented here, phosphorus does affect the microstructural features. Phosphorus has a harmful effect on the mechanical properties of Zircaloy-4 for phosphorus contents over 60 ppm (37). However, as shown in Table 2, when the phosphorus content is .59 ppm, the sample contains 50% of 'basketweave-type' microstructure. These observations should prove to be a valuable guide when changing the Zircaloy-4 specifications to include a reference to P content.
5.2 The Influence of the Impurity (C+P+Si) Content on the Microstructural Features of Commercial Zircaloy-4 Nuclear Fuel Cladding

5.2.1 The Microstructure

As is shown in Table 5, the percentage of basketweave structure and the structure which is tending to basketweave, increases with increasing amount of impurities (C+P+Si). As was discussed before, a high impurity content during the $\beta \rightarrow \alpha$ transformation would give more second-phase particles and these particles are distributed randomly over numerous (twelve) habit planes in the prior $\beta$ grains. These particles act as nucleation sites and the plates interweave each other. The plates in fact radiate out from the second plate particles. Under certain conditions, two samples could end up having the same percentage of basketweave structure although the impurity contents were different. However, as can be seen when comparing the microstructures presented in Figures 20(h),(i),(j), a finer structure is produced in the higher impurity (C+P+Si) content material. In this regard carbon is particularly effective in promoting a fine structure. It is worth noting that according to empirical equations in Table 4, it is impossible to produce a basketweave or 'basketweave-type' structure without adding carbon and silicon to Zircaloy-4. It is surprising that phosphorus (in combination with C+Si) did not positively promote B, B+Tb structures but in fact acted against C+Si and made it more difficult to form 'basketweave-type' or/and basketweave structure. It would
therefore suggest that if the phosphorus content is increased, one should also add a significant amount of C and Si in order to compensate for the inhibition effect of phosphorus on B or B+Tb formation. This is of course at odds with our results obtained for Zircaloy-P alloys where the C+Si+O+N is constant and one varies the phosphorus content. The most reasonable explanation is that the phosphorus content is rather low in these 10 batches of fuel sheathing and its effect is 'masked' by the greater effects of C, Si and cooling rate. Undoubtedly, the phosphorus-containing particles positively identified by EELS (6) have proven to act as 'basketweave-type' structure nucleation sites (4,6). Although the diffraction pattern of a complex phosphide, \( \text{Zr}_3\text{P} \), has not been fully indexed, a quantitative analysis using the electron microprobe (36) coupled with SAD patterns showed that the crystallography of phosphide could be either cubic or hexagonal.

As it has been shown with respect to the major impurities (C,P,Si,O,N) listed in Table 1, the impurity content can be correlated very well with the formation of a basketweave type microstructure with a high impurity(ies) content giving a high percentage of 'basketweave-type' structure. Taking as an example the Zircaloy-4-P alloy, the empirical equations with phosphorus as independent variable demonstrate that the higher impurity the higher the percentage of 'basketweave-type' and the finer the structure. Metallographically, it can be seen that although phosphorus contributes to an increase in the amount of the 'basketweave-type'
structure, it is not a major factor in producing a finer structure.

With respect to Si, it also gives an increase in basketweave structure and fineness of structure. It is however not so visible metallographically as P. From the published literature (16,39), it appears that the silicon could exist in either an elemental or a compound form in the zirconium alloy. A Zr-Si compound might be the product of the raw material (ZrSiO₄) used in the Kroll process for zirconium production. The most likely phase to form is Zr₄Si. However, its phase identification is still uncertain. Zr₄Si has been identified by SAD patterns and its crystallography is reported to be either hexagonal or tetragonal. Si powder could be intentionally added at the arc melting stage as fairly coarse particles and remain at the elemental form. There are a number of reasons in addition to its refining effect on the Widmanstatten structure for adding Si to the zirconium sponge.

It also contributes to high-temperature strength via dynamic strain aging in titanium alloys (Titanium 4wt%Al-4wt%Mg-2wt%Sn) (40). Si is also added during the steel refining processes or to zirconium sponge to eliminate or maintain the oxygen content as low as possible, because oxygen has been reported (41) as a matrix embrittlement factor in Zircaloy-4. However a certain level of oxygen is beneficial since for Zircaloy-4
it refines the structure (14). The maximum amount of oxygen in Zircaloy-4 is specified at about 1500 ppm, since higher contents will degrade the mechanical properties.

The empirical equations developed from this study indicate that the most effective method to promote 'basket-weave type' or basketweave structure is to increase the carbon and/or silicon content (Eqs. (6), (7), (11), Table 4). This is in agreement with the earlier predictions of Fong and Northwood (16).

5.2.2 Grain Size

According to the specification No. NP-M-1007, outlined and imposed by Atomic Energy of Canada Limited (42), the average grain size of the finished Zircaloy seamless tubing (prior to attachment of appendages) should not exceed 10 μm and no grain should be larger than 25 μm. It is evident, e.g., Figure 10, all as-received condition materials regardless of (C+Si+P) content had a grain size in accord with this specification requirement. However, as mentioned earlier, the grain size in Zircaloy-4 fuel cladding prior to the brazing process is affected by the impurity (C+P+Si) content with the result that increasing the impurities content decreases the grain size. A small grain size is preferred since a large grain size would increase SCC susceptibility from fission (iodine) product at elevated temperatures which is known to be a probable cause of fuel element failures (35). As one can see from Table 6, the prior-β grain size is over 300 μm for all materials that have undergone the simulated
brazing treatment. Thus they do not fulfill the requirement of at least three grains through the wall thickness of the Zircaloy-4 fuel cladding. As mentioned previously, the simulated brazing times used here are much longer than in the practical situation and the brazing time significantly affects the grain size (15). With respect to these measured grain sizes, it is probably useful to examine the grain size measurement method used here. Briefly, the grain sizes given in Table 6 are the averages obtained from 60 to 100 grains in one sample. Looking at the histogram of grain sizes for the air cooled sample containing 171 ppm C+P+Si (Figure 14), the variation of grain sizes is quite large and with the highest frequency of occurrence being for grains with a diameter of 210\(\mu\)m. Furthermore, 50% of the grains in this sample are distributed between 150-300\(\mu\)m. Therefore, the average grain size is better given as 300±90\(\mu\)m rather than 350\(\mu\)m. The impurity content of the sample does affect the grain size, although it is not a strong effect.

Holt (4) states that the mechanism for the formation of the basketweave structure (\(\beta+\alpha\)) in Zr-4 is by a nucleation process rather than growth process, because the grain sizes did not change that much with variation the experimental temperature. In low carbon steel, as shown in Figure 26, the grain size does not change too much if the temperature (the austenite temperature) is kept in certain range because the manufacturer adds a small amount of Al into the steel to minimize grain growth. Usually the low carbon steel ingot is hot forged into billets and machined into gears, then the
gears are surface hardened by gas carburizing. Unfortunately, if the heat treatment temperature exceeds a certain value, then the grains grow rapidly (Figure 26), and the final product is rejected. This phenomenon is similar to that in Zr-4, where the grain size in the braze affected zone of Zr-4 change gradually with the brazing time/temperature, but do not grow rapidly because the impurities (C+P+Si) acts as grain growth inhibitors similar to Al in low carbon steel. If the brazing temperature exceeded a certain value, the grains would grow rapidly. The above description is intended to illustrate why grain size might not be a major factor in determining the $\beta + \alpha$ mechanism in Zr-4 because, as is evident from this work (Table 6). Thus the grain size could be kept within specification by control of the impurity (C+P+Si) content providing the brazing temperature and time are also properly controlled. The empirical equations given by SAS analysis (Equation 10, Table 4) indicate that the grain size is decreased with increasing the impurity (C & Si) content, but the effect of P is limited. Figure 13 in which GS is plotted against (C+P+Si) content, the limited effect of impurity content on grain size is illustrated. Carbon seems to be the most effective in producing a finer structure.
In summary, the favorable grain size refining elements are carbon and silicon. A high phosphorus content is not recommended since not only does it make the alloy unworkable but also it is reported (36) that any alloying element which modifies the concentration of carbon in solid solution may affect the phosphorus segregation, even if there is no direct interaction between the alloying element and phosphorus.

5.2.3 Plate Width (PW) and Plate Length (PL)

a) PW

The present data show that PW varies with the impurity content, especially with the P and Si contents. PW decreases if one increases the impurity content and increasing the P+Si content is particularly favorable. The SAS empirical equation developed from the present work predicts that PW is about 34 $\mu$m if there is no C+P+Si present and the cooling rate is infinitely slow. The experimental observations show that the 'parallel-type' plate does not exist if the sample contains 298 ppm (C+P+Si) or more. This does not agree exactly with SAS's predicted values. However, both SAS analysis and experimental observations show that in the sample containing 393 ppm no Pa would be formed. This impurity content (C+Si +P = 393ppm) is the highest impurity (C+P+Si) content for the ten batches of seamless Zircaloy-4 tubing tested here.

Since the Zircaloy-4 tubing is required to withstand stresses in service, it is important to be able to correlate tensile properties with the microstructure (43). Lustman and Kerze (44) have emphasized the importance of grain size and the additive nature of the strengthening processes in
Zirconium. It is demonstrated in Figure 27 very clearly for our own results that a larger grain size promotes not only a higher percentage of 'parallel-type' microstructure, but gives a coarser plate width. All of these factors related to a large grain size should produce a degradation in mechanical properties. According to Warren and Beevers' (45) an increased grain size and a decreased oxygen content favours the formation of fatigue damage in association with these \(\{11\overline{2}1\}\) twins in zirconium alloys. In nitriding pearlitic steel, it is the author's experience that the 'fish eye' feature appearing in the nitriding steel after a fatigue test is small only if the pearlite spacing is small. Thus the fatigue strength is higher in the finer spacing materials. Therefore, the total impurity content, which includes C+P+Si and oxygen would contribute to increasing the Zircaloy-4 fatigue strength. Increasing the impurity content would reduce fatigue damage because, according to Armstrong and Horne (46) the twins could provide the matrix hardening and barriers required to cause the dislocation coalescence which would lead to fatigue cracking because the internal twinning is observed at fast cooling rate \((\sim 2000^\circ C/s)\) for the sample containing the lowest oxygen content \((0.13\text{wt\%})\) (14) (Eq. (8), Table 4). As indicated the SAS analysis, the major factor in producing a finer structure, i.e., smaller FW, is increased phosphorus rather than the other factors such as C, Si, or CR. It is interesting to compare this observation with that of Wilkinson et al (47) who found that additions of phosphorus, manganese and silicon to \(2.25\%\text{Cr}-1\%\text{Mo}\) steels produced a marked
increase in rupture ductility at 550°C. Pilling et al (48) who showed that phosphorus promoted an increase in the minimum creep rate of 2.25%Cr-1%Mo steels at stresses between 80 and 120 MPa, with the magnitude of the increase being dependent on the carbon content of the steel. The literature (44, 45) describes exactly as same as the empirical equation (eq. 8, Table 4) predicts. In conclusion, the creep strength and fatigue strength would be expected to increase with a decreasing plate width produced by increasing the impurity content. Creep has been shown to cause the sheathing failure during a so-called LOCA (Loss of Coolant Accident) (49). In the event of a loss of coolant accident, internal fission gas pressure can cause the cans to "balloon". If the strain to failure is high, ballooning of adjacent fuel rods may reduce the sub-channel flow area available for the emergency coolant.

b) PL

As can be seen in Figure 16, a plot of PL vs. (C+P+Si) shows considerable scatter with the error of measurement being large when PL is measured at high magnifications. In order to obtain representative data for PW and PL, one should measure all the plates which are present in one area rather than measure few of them. Generally about 200 plates are measured in one sample. The plates are difficult to measure because of Tp, the tending to parallel-plate structure, and the associated uncertainty of length. The empirical equation (Equation 9, Table 4) which related PL to impurity content and cooling rate is likely to contain 'errors' due to these
uncertainties in measuring PL. The PL empirical equation should however have the same format as that for PW, that is:

$$PL(\mu m) = 405.88 - 1.04C - 0.84P - 0.50Si - 0.020CR$$

Basically, PL is decreased with increasing impurity content. A shorter PL is preferred because cracks can run along plate boundaries at 400μm. It can run completely through the wall of the sheathing.

5.3 The Influence of Cooling Rate on the Microstructural Features

The cooling rates examined were: furnace cooling (0.01°C/s), air cooling (100°C/s), oil quench (750°C/s), water quench (5000°C/s), brine quench (5700°C/s) and dry-ice acetone quench (7000°C/s). The cooling rates are calculated from AECL (Atomic Energy of Canada Limited) published data (50).

5.3.1 The Structures

Undoubtedly, the type of microstructure developed is greatly dependent on the cooling rate. A high percentage of basketweave structure and fine structure is obtained at a faster cooling rate. This is illustrated in Figure 21 for a sample containing 393 ppm (C+P+Si) where the structure changes gradually as the cooling rate changes from slow cooling to rapid cooling. More B is obtained at high cooling rate. A 100% basketweave structure was only obtained by air cooling in the sample with the highest impurity content. The basketweave structure is finer after water quenching.
than after air cooling. A martensitic structure could be seen when the $\beta + \alpha$ transformation sample was cooled in water or in another media having a faster cooling rate than water.

The zirconium-rich end of the binary zirconium-tin phase diagram is shown in Figure 28. It indicates that the solubility of tin is very small in alpha zirconium and considerably larger in beta zirconium. Quenching dilutes alloys of appropriate compositions from the beta field at rapid rates should bring about the martensitic beta to alpha prime transformation and in view of the extremely restricted solubility of tin in the alpha phase, the martensite would be supersaturated. If the cooling rate is not fast enough, it is possible that a fraction of the tin atoms would be thrown out of the zirconium lattice. Precipitation would occur during the quenching process. Progressive additions of tin would be expected to lower the $M_s$ temperature. The tin concentration would be increased at higher temperature, and less martensitic structure would be formed if the cooling rate is the same. However, it is impractical to depress the formation of martensitic structure by increasing the temperature because it also would increase the grain size and the amount of zirconium carbide would increase simultaneously with increasing tin concentration. With the result that phosphorus would segregate along the grain boundaries due to the lack of carbon (13,36). The alloy would then be very brittle. Returning to the empirical equations in Table 4, as the cooling rate is varied from
0.01°C/s to 7000°C/s, the amount of 'basketweave-type' microstructure is not strongly affected by cooling rate (Eqs. (6), (7), Table 4). However, the cooling rates are calculated from published curves and may be in error. For instance, if we take Woo and Tangri's (14) work, the cooling rate for water quenching was estimated as approximately 1500°C/s which is to be compared with the figure 5000°C/s of this work, i.e., almost five times different. If we could measure the cooling rates by experimental methods then the empirical equation which include cooling rate as an independent variable would better show the effect of CR on 'basketweave-type' structure or the other microstructural features.

5.3.2 GS, PW and PL

In general, GS, PW and PL become smaller, finer and shorter with increasing cooling rate. The phenomenon has been described in detail previously. It is considered that the intercept of PW in Equation (8) of Table 4 should be higher than the predicted value and the multiplying factors for carbon and silicon should also be higher than the predicted values. However, Carbon content is a major factor controlling the fineness of the microstructure (as is evident from the experimental work).

In summary, from the data presented CR is not a major factor because one can obtain a 100% basketweave structure by air cooling if the impurity content is high enough. However, should the impurity content of the sheathing be marginal for forming the required structure, then an increase in cooling
rate from the brazing temperature would be beneficial.

5.4 Implications

According to Okvist and Kallstrom's work (3), a basketweave structure would be obtained if the carbon content in the sample is over 100 ppm. According to the present work the percentage of basketweave structure would increase gradually with increasing (C+P+Si) content and would be 100% basketweave structure if the impurity content is 200 ppm. It would be impractical to raise the phosphorus content to 200 ppm to get 100% of basketweave structure because for phosphorus contents over 100 ppm, the alloy will crack along the grain boundaries after \( \beta \rightarrow \alpha \) transformation. Carbon and phosphorus are very competitive elements in metals and if the phosphorus content is increased and the amount of tin or iron increases, then carbon will go to the grain boundaries to combine with the Fe/Sn in solution to form carbides (36). Silicon has been shown to improve the mechanical properties of an \( \alpha + \beta \) titanium alloy (40) which is similar in its physical metallurgy in many respects to zirconium alloys. Although phosphorus does increase the creep strength in 2.25%Cr-1%Mo steels (48) it is not a recommended addition in large amounts. From the literature available (16,36,40,48) and the thermal treatments in the present work, carbon and silicon are the most desirable elements for a positive effect on the microstructural features in Zircaloy-4 fuel cladding. However, one can
see the beneficial effect of phosphorus on PL and PW. Therefore, the phosphorus content in the specification presently (<20 ppm) could be revised and increased to about 50 ppm. At this phosphorus level, approximately 45% of 'basketeave-type' structure is obtained even in absence of significant amounts of C or Si.

5.5 SAS Empirical Equations

As the present data shows, phosphorus has a positive effect on the microstructural features of Zircaloy-4 in the case where there is a scarcity of other impurity elements such as C and Si. The general form of the SAS empirical equations can be written as follows:

\[
\begin{align*}
GS, PW, PL &= C_1 - F(P) \quad C_1 \neq C_2 \quad C_1 > C_2 \\
B, B+Tb &= -C_2 + F(P) \quad C_1 \neq C_2 \neq 0 \\
GS, PW, PL &= C_3 - F(C, P, Si, CR) \quad C_3 \neq C_4 \neq 0 \\
B, B+Tb &= -C_4 + F(C, P, Si, CR) \quad C_3 > C_4
\end{align*}
\]

where \( F \) indicates 'some function of'.

In more general terms:

\[
\begin{align*}
GS, PW, PL &= \text{constant} - F(\text{impurity content}) \\
B, B+Tb &= -\text{constant} + F(\text{impurity content}).
\end{align*}
\]

The desirable conditions for the formation of a high percentage of the basketeave structure are either that the grains contain abundant second-phase particles randomly distributed on numerous habit planes, and/or there is an increase in the amount of undercooling as obtained with increase in cooling rate (c.f., Equation 4).
CHAPTER 6

Conclusions

1) The percentage of the 'basketweave-type' structure increases with increasing impurity (C+P+Si or P) content.

2) Grain size (GS), plate width (PW) and plate length (PL) decrease as the impurity (C+P+Si or P) content is increased.

3) The cooling rate (furnace cooling, air cooling, oil quench, water quench, brine quench and dry ice-acetone quench) affects the microstructural features of Zircaloy-4, but the effect is weak when compared to that of the impurity content.

4) The cooling rate is more important in PL and GS than in controlling (B+Tb) and PW.

5) The effect of the impurities on the microstructural features of Zircaloy-4 can be ranked as follows from the most important to the least important: C, Si, P.

6) SAS analysis has been used to develop relationships between the independent variables (impurity contents and/or cooling rates) and the dependent variables (%B, %B+Tb, GS(µm), PW(µm), PL(µm)) and these are given in the form of empirical equations in Table 4.

7) In general, neglecting the effects of cooling rate, the empirical equations can be written as follows:

\[ B, B+Tb = -\text{Constant (1)} + F(\text{impurity content}) \]  

\[ \text{GS, PW, PL = Constant (2)} - F(\text{impurity content}) \]
where, $\text{Constant}_{(1)} \neq \text{Constant}_{(2)} \neq 0$,

$\text{Constant}_{(1)} < \text{Constant}_{(2)}$.

8) The phosphorus content in Zircaloy-4 could be beneficially increased to approximately 50 ppm from the level of less than 20 ppm in the present specification.

9) Depending on the thermal treatment, Zircaloy-4 becomes very brittle and cracks along prior-β grain boundaries if the phosphorus content is over 100 ppm.

10) In order to ensure the quality of Zircaloy-4 fuel cladding at brazing affect zone, the cooling rate of the brazing metal should be approximate to oil quenching (~750°C/s). Microstructurally, this cooling rate is the best.
CHAPTER 7

Suggestions for Future Research

It would seem worthwhile to study the effect of varying the silicon content and while keeping the $2P+O+N$ content constant. The microstructural features would be analyzed quantitatively and the effect of independent variation of Si content would be determined. It is also suggested that a series of Zircaloy-4 melts be prepared, similar to those for this study with high P content, where the total impurity C+P+Si content is varied. A quantitative analysis of the microstructural features is then made. Tensile and hardness tests would be performed and the properties related to microstructure. As a result of these studies it would be hoped that the specification for Zircaloy-4 nuclear fuel-cladding could be modified to give overall better properties. In addition, creep tests could be carried on materials with the modified specification to determine the beneficial detrimental effects of the specification change.

Based on the present results, it is suggested that the carbon content is increased to 250 ppm whilst the phosphorus content is maintained at below 60 ppm. At that level of phosphorus, the 'basketweave-type' microstructure is approximately 50% and the harmful effect of higher phosphorus contents is avoided. SAS's linear model program could be applied to analyze all the data available and develop a computer program which will predict an optimum impurity content range in Zircaloy-4. This impurity content range would

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not only give desirable microstructural features but also
give good mechanical properties. The reason for the poor
mechanical properties (if any) of 'homemade' Zircaloy-4
could be found using x-ray, SEM, TEM, or an etching method
which would show the distribution of the different kind of
the second-phase particles by colour differences under the
optical microscope. Such a project would not only be
important from an academic standpoint but also from an
applied technology aspect since it would act as a guide in
alloy design.
REFERENCES


50. W.M. Rumball, "Hardenability of Zr-1.2wt%Cr-0.1wt%Fe," Atomic Energy of Canada Limited, AECL-3050, 1968.
Table 1

Analysis of The Impurity Contents in Zircaloy-4 Fuel Cladding

<table>
<thead>
<tr>
<th>Tube Identification</th>
<th>C+P+Si (ppm)</th>
<th>Impurity Content (ppm by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>171</td>
<td>130</td>
</tr>
<tr>
<td>B</td>
<td>195</td>
<td>150</td>
</tr>
<tr>
<td>C</td>
<td>393</td>
<td>260</td>
</tr>
<tr>
<td>D</td>
<td>322</td>
<td>245</td>
</tr>
<tr>
<td>E</td>
<td>273</td>
<td>180</td>
</tr>
<tr>
<td>F</td>
<td>231</td>
<td>140</td>
</tr>
<tr>
<td>G</td>
<td>298</td>
<td>190</td>
</tr>
<tr>
<td>H</td>
<td>270</td>
<td>170</td>
</tr>
<tr>
<td>I</td>
<td>151</td>
<td>120</td>
</tr>
<tr>
<td>J</td>
<td>181</td>
<td>150</td>
</tr>
</tbody>
</table>
### Table 2

A Summary of the Quantitative Analysis of the Microstructural Features of Zircaloy-4-P Alloys

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>Phosphorus Content (ppm)</th>
<th>Type of Microstructure†</th>
<th>GS⁺ (μm)</th>
<th>PW⁺ (μm)</th>
<th>PL⁺ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁</td>
<td>42</td>
<td>43 9 29 98 19</td>
<td>1409</td>
<td>24.6</td>
<td>406</td>
</tr>
<tr>
<td>M₂</td>
<td>59</td>
<td>40 10 25 50 25</td>
<td>1390</td>
<td>24.2</td>
<td>459</td>
</tr>
<tr>
<td>M₃</td>
<td>78</td>
<td>39 10 30 81 21</td>
<td>1353</td>
<td>21.3</td>
<td>399</td>
</tr>
<tr>
<td>M₄</td>
<td>89</td>
<td>25 17 34 58 24</td>
<td>1323</td>
<td>19.9</td>
<td>384</td>
</tr>
<tr>
<td>M₅</td>
<td>103</td>
<td>28 12 34 60 26</td>
<td>1317</td>
<td>17.2</td>
<td>330</td>
</tr>
<tr>
<td>M₆</td>
<td>128</td>
<td>18 11 26 71 45</td>
<td>1297</td>
<td>15.2</td>
<td>338</td>
</tr>
<tr>
<td>M₇</td>
<td>160</td>
<td>9 2 29 89 60</td>
<td>1290</td>
<td>14.3</td>
<td>241</td>
</tr>
</tbody>
</table>

† Tp = Tendency to parallel plate  
Pa = Parallel plate  
Tb = Tendency to basketweave  
B = Basketweave  
GS = Grain Size  
PW = Plate Width  
PL = Plate Length
Table 3
Description of α-Widmanstatten structures in Zircaloy-4

<table>
<thead>
<tr>
<th>Structure+</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tp</td>
<td>Most of the nucleation sites are such that the precipitates are on one habit plane in prior-β grains. These are referred to as discontinuous plates. However it is still 'parallel-plate type' microstructure (Examples in Figure 3(a), 4(a)).</td>
</tr>
<tr>
<td>Pa</td>
<td>Short and continuous plates. Prior-β grain boundary is the favourable nucleation site. (See Figure 3(b)).</td>
</tr>
<tr>
<td>Tb</td>
<td>Non-parallel and randomly distributed plate structure. Nucleation sites such that precipitation is on numerous habit planes in prior β grains. The result is that the plates interweave one another. (See Figure 3(c), 4(c)).</td>
</tr>
<tr>
<td>B</td>
<td>It is different from Tb in that the plates interweave other plates perfectly. (See Figure 3(d), 4(d)).</td>
</tr>
<tr>
<td>M</td>
<td>It is formed at rapid cooling rates (faster than water quenching when the impurity (C+P+Si) content of the sample is 231 ppm or lower. A needle-like structure similar in appearance and of formation to the ferrous martensites. Formed by diffusionless transformation. (See Figure 3(e)).</td>
</tr>
</tbody>
</table>

+ Tp = tendency to parallel plate structure  
Pa = parallel plate structure  
Tb = tendency to basketweave structure  
B = basketweave structure  
M = martensitic structure
Table 4

SAS's Empirical Equations Developed on the Basis of Quantitative Metallography

<table>
<thead>
<tr>
<th>Independent Variable*</th>
<th>Dependent Variable</th>
<th>Empirical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Grain Size</td>
<td>GS(µm) = (1440.021±17.722)-(1.064±0.175)P</td>
</tr>
<tr>
<td></td>
<td>Plate Width</td>
<td>PW(µm) = (28.899±1.140)-(0.10±0.011)P</td>
</tr>
<tr>
<td></td>
<td>Plate Length</td>
<td>PL(µm) = (513.933±32.110)-(1.579±0.317)P</td>
</tr>
<tr>
<td></td>
<td>Tb+B (%)</td>
<td>Tb+B(%) = (28.204±4.444)+(0.348±0.044)P</td>
</tr>
<tr>
<td></td>
<td>B (%)</td>
<td>B(%) = -(0.97±6.921)+(0.344±0.068)P</td>
</tr>
<tr>
<td>C,P,Si,CR</td>
<td>B</td>
<td>B(%) = -(102.125±15.460)+(0.719±0.124)C-(0.358±0.328)P+(0.258±0.106)Si+(0.004±0.001)CR</td>
</tr>
<tr>
<td></td>
<td>B+Tb (%)</td>
<td>B+Tb(%) = -(8.439±6.065)+(0.411±0.049)C-(0.312±0.129)P+(0.243±0.042)Si+(0.001±0.000)CR</td>
</tr>
<tr>
<td></td>
<td>Plate Width</td>
<td>PW(µm) = (34.287±16.689)-(0.048±0.127)C-(0.346±0.534)P-(0.020±0.104)Si-(0.003±0.001)CR</td>
</tr>
<tr>
<td></td>
<td>Plate Length</td>
<td>PL(µm) = (405.876±137.709)-(1.037±1.048)C+(0.845±4.410)P-(0.501±0.857)Si-(0.021±0.005)CR</td>
</tr>
<tr>
<td></td>
<td>Grain Size</td>
<td>GS(µm) = (474.217±24.305)-(0.443±0.195)C+(0.094±0.515)P-(0.332±0.167)Si-(0.009±0.001)CR</td>
</tr>
<tr>
<td>C,P,Si</td>
<td>B+Tb (%)</td>
<td>B+Tb(%) = -(6.583±9.398)+(0.453±0.077)C-(0.324±0.202)P+(0.140±0.01066)Si</td>
</tr>
<tr>
<td></td>
<td>Grain Size</td>
<td>GS(µm) = (432.378±14.966)-(0.385±0.122)C+(0.071±0.322)P-(0.292±0.104)Si</td>
</tr>
<tr>
<td></td>
<td>Plate Width</td>
<td>PW(µm) = (21.865±3.367)-(0.303±0.026)C-(0.370±0.108)P+(0.003±0.021)Si</td>
</tr>
<tr>
<td></td>
<td>Plate Length</td>
<td>PL(µm) = (450.867±64.215)-(1.549±0.491)C-(3.128±2.063)P-(0.340±0.395)Si</td>
</tr>
</tbody>
</table>

* C,P,Si,CR = Carbon, Phosphorus, Silicon, Cooling Rate
(C,P,Si) in µm; CR in °C/s.
<table>
<thead>
<tr>
<th>Cooling Rate</th>
<th>Type of Microstructure (%)</th>
<th>Tube Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>Tp</td>
<td>40 29 5 7 25 30 13 14 42 30</td>
</tr>
<tr>
<td></td>
<td>Pa</td>
<td>12 12 6 6 10 17 .9 15 15 18</td>
</tr>
<tr>
<td></td>
<td>Tb</td>
<td>48 59 45 42 54 51 41 54 43 52</td>
</tr>
<tr>
<td>0.01°C/s</td>
<td>B</td>
<td>44 45 11 2 37 17</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>Tp</td>
<td>37 29 12 33 13 12 30 27</td>
</tr>
<tr>
<td>Cooling</td>
<td>Pa</td>
<td>6 8 5 8 3 25 11</td>
</tr>
<tr>
<td>100°C/s</td>
<td>Tb</td>
<td>48 46 61 42 54 36 50</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>9 17 100 100 22 17 87 31 9 12</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Oil Quench</td>
<td>Tp</td>
<td>31 28 16 30 11 10 36 32</td>
</tr>
<tr>
<td>750°C/s</td>
<td>Pa</td>
<td>9 3 3 9 5 10 8</td>
</tr>
<tr>
<td></td>
<td>Tb</td>
<td>50 49 30 58 52 45 43</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>10 20 100 100 51 3 89 33 9 17</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Water Quench</td>
<td>Tp</td>
<td>22 24 9 24 4 24 25</td>
</tr>
<tr>
<td>5000°C/s</td>
<td>Pa</td>
<td>15 10 6 14 3 20 12</td>
</tr>
<tr>
<td></td>
<td>Tb</td>
<td>30 44 42 46 59 39 41</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>27 17 100 100 43 16 100 34 11 19</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>6 5</td>
</tr>
</tbody>
</table>

... Cont'd.
Figure 10: As-received structures of Zircaloy-4 fuel cladding.
(a) The lowest impurity content (C+Si=151 ppm).
(b) The highest impurity content (C+Si=393 ppm).
Table 6

Summary of the Microstructural Features (GS, PW, PL) Measurement for Zircaloy-4 Nuclear Fuel Cladding

<table>
<thead>
<tr>
<th>Cooling Rate (°C/s)</th>
<th>Microstructural Feature (µm)</th>
<th>C</th>
<th>D</th>
<th>G</th>
<th>E</th>
<th>H</th>
<th>F</th>
<th>B</th>
<th>J</th>
<th>A</th>
<th>I</th>
<th>Av.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furnace Cooling (0.01)</td>
<td>GS</td>
<td>393</td>
<td>417</td>
<td>399</td>
<td>435</td>
<td>428</td>
<td>447</td>
<td>441</td>
<td>464</td>
<td>458</td>
<td>475</td>
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<tr>
<td></td>
<td>PW</td>
<td>36.3</td>
<td>32.5</td>
<td>41.9</td>
<td>41.9</td>
<td>44.0</td>
<td>50.6</td>
<td>42.3</td>
<td>53.8</td>
<td>43.1</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>PL</td>
<td>263</td>
<td>381</td>
<td>439</td>
<td>443</td>
<td>319</td>
<td>546</td>
<td>278</td>
<td>381</td>
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</tr>
<tr>
<td>Air-Cooling (100)</td>
<td>GS</td>
<td>316</td>
<td>328</td>
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<td>338</td>
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<tr>
<td></td>
<td>PW</td>
<td>10.9</td>
<td>9.5</td>
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<td>11.3</td>
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<td>PL</td>
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<td>158</td>
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</tr>
<tr>
<td>Oil Quench (750)</td>
<td>GS</td>
<td>310</td>
<td>322</td>
<td>313</td>
<td>344</td>
<td>334</td>
<td>358</td>
<td>351</td>
<td>363</td>
<td>357</td>
<td>363</td>
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</tr>
<tr>
<td></td>
<td>PW</td>
<td>6.4</td>
<td>6.3</td>
<td>8.1</td>
<td>9.1</td>
<td>9.2</td>
<td>7.3</td>
<td>9.9</td>
<td></td>
<td></td>
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<td>131</td>
<td>121</td>
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</tr>
<tr>
<td>Water Quench (5000)</td>
<td>GS</td>
<td>293</td>
<td>318</td>
<td>303</td>
<td>335</td>
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<td>PW</td>
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<td>6.8</td>
<td>7.7</td>
<td>6.5</td>
<td>8.3</td>
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Figure 1  Parallel plates grow out from other parallel plates in the prior-β grains. (a) The sample contains 195 ppm C+P+Si, water quench. (b) The sample contains 171 ppm C+P+Si, Dry ice-acetone quench.
Figure 2  Vacuum arc melting furnace.
Figure 3 Type of α-Widmanstatten structure formed in Zircaloy-4 fuel cladding after 5 minutes brazing cycle at 1100°C.
(a) Tendency to parallel plate structure. Sample containing 151 ppm of C+P+Si, oil quench.
(b) Parallel plate structure. Sample containing 151 ppm of C+P+Si, water quench.
(c) Tendency to basketweave structure. Sample containing 273 ppm of C+P+Si, oil quench.
(d) Basketweave structure. Sample containing 195 ppm of C+P+Si, air cooling.
(e) Martensitic structure: Sample containing 151 ppm of C+P+Si, dry ice plus acetone quench.
Figure 4  Type of α-Widmanstätten structure formed in Zircaloy-4-P alloys after air cooling from 1100°C for 15 minutes.
(a) Tendency to parallel-plate structure. Sample containing 59 ppm P.
(b) Parallel plate structure. Sample containing 103 ppm P.
(c) Tendency to basketweave structure. Sample containing 59 ppm P.
(d) Basketweave structure. Sample containing 103 ppm P.
Figure 5. Homogenization treatment as applied to cast Zircaloy-4-P alloys.
(a) As-cast structure.
(b) After homogenization treatment at 1100°C for 15 minutes.
Figure 6  The relationship between phosphorus content and the (B+Tb)\% structure for Zircaloy-4-P.
Figure 7 The relationship between phosphorus content and prior-β grain size for Zircaloy-4-P.
Air Cooled

$$PL(\mu m) = (513.933 \pm 32.110) - (1.579 \pm 0.317)P$$

Figure 8 The relationship between phosphorus content and plate length for Zircaloy-4-P.
Figure 9 The relationship between phosphorus content and plate width for Zircaloy-4-P.

Air Cooled

\[ PW(\mu m) = (28.899 \pm 1.140) - (0.10 \pm 0.011)P \]
Figure 10 As-received structures of Zircaloy-4 fuel cladding.
(a) The lowest impurity content (C+P+Si=151 ppm).
(b) The highest impurity content (C+P+Si=393 ppm).
Figure 11 Martensitic structure of Zircaloy-4 fuel cladding after brazing for 5 minutes and then cooling in dry ice acetone solution.

(a) Specimen containing 151 ppm of C+P+Si.
(b) Specimen containing 195 ppm of C+P+Si.
(c) Specimen containing 231 ppm of C+P+Si.
Figure 12 The relationship between the impurity content and (B+Tb) structure for Zircaloy-4.
Figure 13  The relationship between the total impurity content and the measured grain size for six cooling rates for Zircaloy-4.
Figure 14: The histogram of the sample containing 171 ppm (C+P+Si) for air cooled Zircaloy-4.
Figure 15  The plot of the measured data of the plate width vs. the impurity (C+P+Si) content for Zircaloy-4.
Figure 16  The plot of the computed data of the plate width vs. the impurity (C+P+Si) content for Zircaloy-4.
Figure 17  The relationship between the impurity (C+P+Si) content and plate length of the air cooled material for Zircaloy-4.
Figure 18 The relationship between the impurity (C+P+Si) content and grain size of the air cooled material for Zircaloy-4.

$\text{GS (\text{\mu m})} = (432.082 \pm 14.966) - (0.385 \pm 0.122)C + (0.071 \pm 0.322)P - (0.292 \pm 0.104)Si$
Figure 19 The relationship between the impurity (C+P+Si) content and plate width of the air cooled material for Zircaloy-4.

\[ PW(\mu\text{m}) = (21.865 \pm 3.367) - (0.037 \pm 0.026)C - (0.370 \pm 0.108)P + (0.003 \pm 0.021)Si \]
Figure 20  The influence of the impurity content on the microstructure of Zircaloy-4 fuel-cladding after air cooling from 1100°C.

(a) C+P+Si = 151 ppm

(b) C+P+Si = 171 ppm
(c) $C+P+Si = 181$ ppm

(d) $C+P+Si = 195$ ppm
(e) C+P+Si = 231 ppm

(f) C+P+Si = 270 ppm
(g) C+P+Si = 273 ppm

(h) C+P+Si = 298 ppm
(i) C+P+Si = 322 ppm

(j) C+P+Si = 393 ppm
Figure 21 The influence of cooling rate on the microstructure of Zircaloy-4 fuel cladding containing $(C+F+Si) = 393$ ppm.

(a) Furnace cooling, (b) Air cooling,
(c) Oil quench, (d) Water quench,
(e) Brine quench, (f) Dry ice-acetone quench.
Figure 22 The relationship between the cooling rate and the grain size for Zircaloy-4.
Figure 23  The relationship between the cooling rate and the plate width for Zircaloy-4.
Figure 24 The relationship between cooling rate and plate length for Zircaloy-4.

\[
P_L (\mu m) = (149.965 \pm 4.991) - (0.004 \pm 0.003)CR
\]
Figure 25 Photograph showing how the shape of metal chips from machining varies with the phosphorus content.
Figure 27 The plot of (GS; Tp+Pa; PW) vs. the impurity content for Zircaloy-4.
Figure 28 Zr-Sn phase diagram
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