February 17, 1984

Docket No. 50-320

(10 C.F.R. 2.206)

Mr. Marvin Lewis
6504 Bradford Terrace
Philadelphia, Pennsylvania 19149

Dear Mr. Lewis:

This is in response to your letter of September 13, 1983, requesting that
the NRC postpone the lifting of the reactor pressure vessel head. On
October 19, 1983, you were informed that your letter would be treated as
a request for action pursuant to 10 C.F.R. 2.206 of the Commission's regula-
tions. Your request was based on your concern regarding the potential
existence of pyrophoric materials within the reactor pressure vessel which
could result in a pyrophoric reaction during the lifting of the reactor
pressure vessel head. Your request was supported by a letter dated
November 1, 1983, from Professor Earl Gulbransen of the University of
Pittsburgh to the Secretary of the Commission.

For the reasons set forth in the enclosed "Director's Decision under
10 C.F.R. 2.206," DD-84-4, your request is denied. A copy of the decision
will be referred to the Secretary for the Commission's review in accordance
with 10 C.F.R. 2.206(c).

Sincerely,

Original Signed by
H. R. Denton

Harold R. Denton, Director
Office of Nuclear Reactor Regulation

Enclosures:
1. Director's Decision
2. Federal Register Notice

cc w/Encls: Dr. Earl Gulbransen

OFFICE ▶	TMIPO:NRR	PD:TMIPO:NRR	ELD	DD:NRR	D:NRR		
SURNAME ▶	RAWeller:bg	BJSnyder	JLieberman	EGCase	HRDenton		
DATE ▶	2/17/84	2/17/84	2/17/84	2/17/84	2/17/84		

NRC FORM 318 (10-80) NRCM 0240   **OFFICIAL RECORD COPY**   USGPO: 1981-335-960

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Docket No. 50-320
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UNITED STATES OF AMERICA
NUCLEAR REGULATORY COMMISSION

OFFICE OF NUCLEAR REACTOR REGULATION
Harold R. Denton, Director

In the Matter of	)	
	)	
GENERAL PUBLIC UTILITIES NUCLEAR	)	Docket No. 50-320
CORPORATION	)	
(Three Mile Island Nuclear Station,	)	
Unit 2)	)	(10 C.F.R. 2.206)

DIRECTOR'S DECISION UNDER 10 C.F.R. 2.206

By letter dated September 13, 1983 to the Secretary of the Commission,
Mr. Marvin Lewis requested that the Commission postpone the lifting of the
reactor pressure vessel head at Three Mile Island Nuclear Station, Unit 2
(TMI-2). Mr. Lewis' letter was supported by a letter dated November 1, 1983,
from Professor Earl Gulbransen of the University of Pittsburgh to the
Secretary of the Commission. Attached to Professor Gulbransen's letter was
a paper on the effects of oxygen, nitrogen and hydrogen on the mechanical
properties of zirconium. Mr. Lewis' letter and the supporting letter from
Professor Gulbransen were referred to the Office of Nuclear Reactor Regulation
for treatment as a petition pursuant to 10 C.F.R. 2.206 of the Commission's
regulations.

I have reviewed the information contained in Mr. Lewis' petition, the infor-
mation in Professor Gulbransen's letter of November 1, 1983, and other
information pertinent to the issues raised by the petition. For the reasons
stated in this decision, Mr. Lewis' request is denied.

Petitioner's Assertion and Request

Mr. Lewis contends that pyrophoric materials[1] may well exist within the reactor pressure vessel (RPV) and that the quantity of these materials is unknown. As a consequence, Mr. Lewis believes that the lifting of the RPV head is a "dangerous maneuver" which could result in a pyrophoric event. Mr. Lewis bases the likely existence of pyrophoric materials within the RPV on the conditions which existed within the vessel during the TMI accident. Mr. Lewis contends those conditions were favorable for the formation of pyrophoric zirconium or zirconium hydride, which can react violently when exposed to air. Consequently, Mr. Lewis requests that the RPV head lift be postponed pending a "public review" of the pyrophoricity issue. Mr. Lewis' contentions are supported by Professor Gulbransen, who also asserts that finely divided zirconium or zirconium hydride may well have been formed during the accident. Given the potential pyrophoricity of these materials, Professor Gulbransen warns that these materials must be kept under water pending further characterization of their pyrophoric nature. He urges that the greatest caution be exercised before proceeding with the RPV head lift.

Staff Review of the Pyrophoricity Issue

By letters dated May 25, May 26, and July 20, 1983, General Public Utilities Nuclear Corporation, the TMI Unit 2 licensee, forwarded to the NRC

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[1] Pyrophoric materials are those which are capable of igniting spontaneously in air.

safety evaluation reports to support the planned reactor vessel Underhead Characterization Study.[2] This study was conducted during the months of August through October 1983 to gather data for the RPV head lift and involved a number of different activities. These activities included the lowering of the water in the reactor vessel to a level approximately one foot below the top of the plenum, see Figure 1, the measurement of the radiation fields underneath the RPV head, the measurement of the radiation fields around the RPV head and service structure, the visual inspection under the RPV head with a TV camera, the measurement of the topography of the core cavity with an ultrasonic device, and the removal of six samples from the core debris bed. Inasmuch as these activities, specifically the lowering of the water level in the reactor vessel, involved the uncovering of equipment (the plenum cover) which was previously covered with water, it was necessary to address in advance the issue of exposing potentially pyrophoric material to air. Accordingly, the issue of pyrophoricity was addressed by the licensee as part of its Underhead Characterization Study. Thereafter, the hazard posed by pyrophoric materials in the TMI-2 reactor vessel was extensively evaluated by the NRC staff in its review and approval of the

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[2] See Letter from B. K. Kanga to L. H. Barrett, 4410-83-L-0098, Underhead Characterization Study (May 25, 1983); Letter from B. K. Kanga to L. H. Barrett, 4410-83-L-0100, Underhead Characterization SER, Core Topography Addendum (May 26, 1983); Letter from B. K. Kanga to L. H. Barrett, 4410-83-L-0133, Underhead Characterization SER, Core Sampling Addendum (July 20, 1983).

Underhead Characterization Study.[3] The staff was particularly concerned with the potential for pyrophoric reactions of materials on the plenum cover and of samples removed from the core debris bed. The staff determined in its safety evaluation that:

(1) the presence of steam (i.e., an oxidizing agent) and the temperature conditions during the accident would make it unlikely that significant quantities of zirconium hydride in a pyrophoric condition were produced during the accident,

(2) the primary system flow dynamics during the TMI-2 accident would not likely have transported large quantities of pyrophoric material, if formed, to the top of the plenum, and

(3) any pyrophoric materials in finely divided form would be dispersed and mixed with inert materials of core debris which would prevent the development of pyrophoric conditions.

Following the staff's approval, the Underhead Characterization Study was conducted by the licensee. As described below, all of the visual observations of the reactor vessel underhead conditions and laboratory analyses of the chemical and pyrophoric properties of samples obtained from components within the reactor vessel and from solids filtered from the reactor coolant support the conclusions reached by the staff in its safety evaluation report.

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[3] Details concerning the staff's review are found in the following letters: Letter from L. H. Barrett to B. K. Kanga, NRC/TMI-83-043, Reactor Vessel Underhead Characterization Safety Evaluation (July 13, 1983); Letter from L. H. Barrett to B. K. Kanga, NRC/TMI-83-053, Response to Core Debris Safety Evaluation Report (SER) (August 19, 1983).

The activities undertaken during underhead characterization to address
pyrophoricity concerns were as follows. As a precaution prior to the lowering
of the water level below the top of the plenum, the licensee conducted a closed
circuit television underwater inspection of portions of the plenum cover and
observed that only an insignificant layer of material, approximately 1 millimeter
in depth, was present on some of the plenum surfaces inspected. This observation
verified the staff's conclusion that it was not likely that significant quantities
of materials had been transported to the top of the plenum during the accident.
Following the visual inspection, the licensee obtained two samples of the material
from the plenum surface and the samples were tested for pyrophoricity by various
attempts to initiate a pyrophoric reaction. The tests included a spark test
(i.e., an attempt to ignite the material with an electrically generated spark)
and a flame test (i.e., an attempt to ignite the material with a propane torch
with approximate flame temperature of 2300° F). The spark test is perhaps the
most reliable test for establishing the pyrophoric characteristics of a material
in question as it provides an initiator (i.e., the spark) for a reaction, if one
can occur. The flame test is an extreme test that would show whether the material
in question has any tendency to ignite at all or whether the material is completely
inert.

For comparison with the tests on the plenum samples, the spark and flame
tests were performed with some "cold" (i.e., commercially available
nonradioactive elements and compounds) materials in powdered form, includ-
ing iron, zirconium, and zirconium oxide. The particle size for the iron
and zirconium powders was 62 microns or less and the particle size for the
zirconium oxide was 125 microns or less. The cold tests demonstrated that

the zirconium powder would ignite for both the spark and flame test; however, the material did not ignite spontaneously in the laboratory at atmospheric pressure and ambient temperature (i.e., approximately 70° F). The powdered iron and zirconium oxide failed to ignite in either the spark or flame tests.

The spark and flame tests on the samples removed from the plenum also failed to ignite the material, indicating the presence of little, if any, pyrophoric material and the absence of any pyrophoric characteristics. In fact, the plenum samples showed no more tendency to ignite than the "cold" iron and zirconium oxide samples. Both the "cold" laboratory tests and the tests on the plenum samples were videotaped by the licensee and the videotapes were reviewed by the NRC staff.

In addition to the pyrophoricity tests described above, the licensee performed chemical analyses of solids filtered from the reactor coolant system and of the thin films scraped from the surfaces of the control rod drive mechanism (CRDM) leadscrews removed from the reactor vessel head. See Figure 1. These analyses indicated the absence of zirconium metal and hydride particles. Based on the visual examinations, analyses and tests which indicate the probable absence of pyrophoric materials on the plenum cover, the NRC approved the lowering of the RPV water level to approximately one foot below the plenum surface, which enabled the licensee to proceed with the underhead characterization effort. The water was lowered to this level to simulate the radiological conditions that will exist for

the RPV head lift. As a result, the plenum cover has been exposed to air since August 20, 1983, without any adverse impact. This condition has been visually confirmed by closed circuit television inspection conducted subsequent to the lowering of the water level. Additionally, the six samples which were removed from the core debris bed have been exposed to air for several months with no indication of pyrophoric reactions.
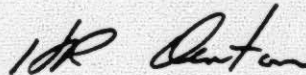
The information resulting from the visual observation of the plenum and the analyses and tests on materials removed from within the RPV indicates that: (1) little material is present on the plenum surface, (2) the material on the plenum surface is not pyrophoric, (3) material filtered from the reactor coolant system during the accident lacks any pyrophoric content, (4) material scraped from CRDM leadscrews lacks any pyrophoric content, and (5) samples of material removed from the damaged core have not shown any tendency to undergo a pyrophoric reaction. Accordingly, the staff concludes that there is little potential for a pyrophoric event with the plenum cover exposed to air. The information provided by Mr. Lewis and Professor Gulbransen is of a general nature concerning pyrophoricity and the dangers that phenomenon poses for the head lift. The staff does not disagree with the petitioner that pyrophoric conditions could have developed in the RPV following the TMI accident. For that reason, prior to the receipt of the petition, the staff considered the issue of pyrophoricity as it relates to the licensee's proposed Underhead Characterization Study. Based upon the staff's reviews and the experience to date as described above, there does not appear to be an undue risk to public health and safety from the possible formation of pyrophoric materials in the pressure vessel.

With regard to Mr. Lewis' and Professor Gulbransen's cautions about proceeding with the RPV head lift on the basis of pyrophoricity concerns, it should be noted that the water level in the reactor vessel is presently at one foot below the plenum cover. This level is precisely that planned for the RPV head lift. No further lowering of the water level is contemplated for the RPV head lift. Thus, no further safety review of pyrophoric issues as related to the head lift is warranted. Moreover this issue has been addressed by actual experience along with evaluations, analyses, tests, and activities performed in connection with the Underhead Characterization Study.

Inasmuch as potential pyrophoric conditions have been given appropriate consideration and do not pose a significant hazard to the head lift, I have determined that no adequate basis exists for postponing the planned lift of the reactor vessel head or initiating proceedings to review the issue of pyrophoricity. Consequently, the petitioner's request is denied.

A copy of this decision wll be filed with the Secretary for the Commission's review in accordance with 10 C.F.R. 2.206(c) of the Commission's regulations.
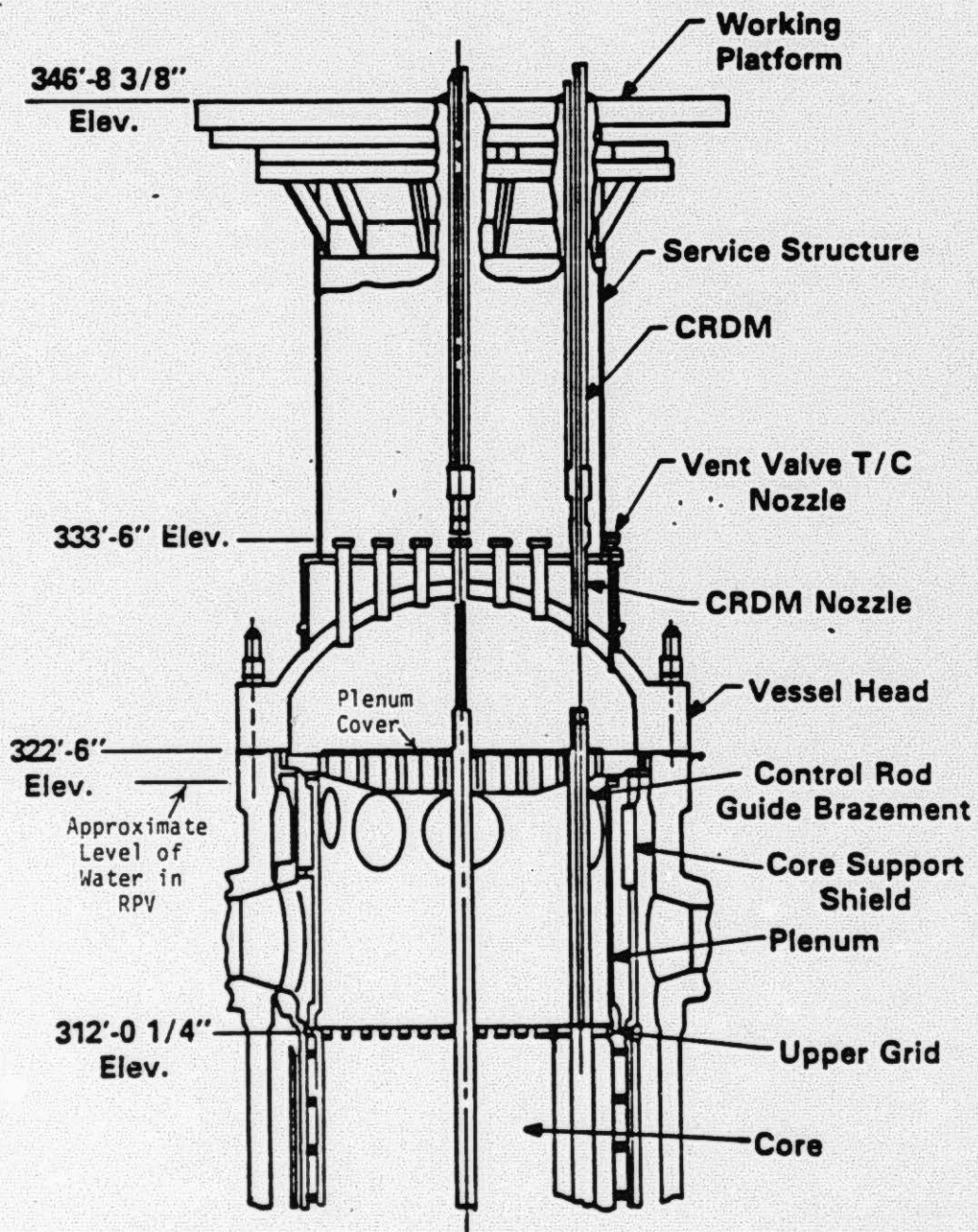
Harold R. Denton, Director
Office of Nuclear Reactor Regulation

Dated at Bethesda, Maryland,
this 17th day of February 1984.

REACTOR & SERVICE STRUCTURE

346'-8 3/8" Elev.

333'-6" Elev.

322'-6" Elev.

Approximate Level of Water in RPV

312'-0 1/4" Elev.

Working Platform

Service Structure

CRDM

Vent Valve T/C Nozzle

CRDM Nozzle

Vessel Head

Control Rod Guide Brazement

Core Support Shield

Plenum

Upper Grid

Core

Plenum Cover

NUCLEAR REGULATORY COMMISSION

[Docket No. 50-320]

GENERAL PUBLIC UTILITIES NUCLEAR CORPORATION

(Three Mile Island Nuclear Station, Unit 2)

Issuance of Director's Decision Under 10 C.F.R. 2.206

Notice is hereby given that the Director, Office of Nuclear Reactor Regulation, has issued a decision concerning a petition dated September 19, 1983, submitted by Marvin Lewis. The petition had requested that the Commission postpone the lifting of the reactor pressure vessel head. The petitioner based his request on the potential existence of pyrophoric materials within the reactor pressure vessel which could result in a pyrophoric reaction during the lifting of the reactor pressure vessel head. The Director, Office of Nuclear Reactor Regulation, has determined to deny the petitioner's request.
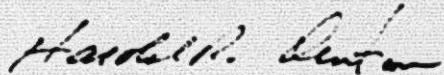
The reasons for this decision are explained in the "Director's Decision under 10 C.F.R. 2.206" (DD-84-4) which is available for public inspection in the Commission's Public Document Room, 1717 H Street, N.W., Washington, D.C., and in the local Public Document Room for the TMI facility, located in the Government Publications Section of the State Library of Pennsylvania,

Education Building, Commonwealth and Walnut Streets, Harrisburg, PA 17126.
A copy of this decision will be filed with the Secretary for the Commission's
review in accordance with 10 C.F.R. 2.206(c).

Dated at Bethesda, Maryland, this 17ᵗʰ day of February 1984.

FOR THE NUCLEAR REGULATORY COMMISSION

Harold R. Denton, Director
Office of Nuclear Reactor Regulation

Secretary of the Commission
UENRC
Washington, D.C. 20555

'03 SEP 15 A10:05

Dear Mr Secretarty :
Please consider the following letter as a petition to stop any headlift for the
TMI#2 reactor. Several parts of the Rules and Regulation of the NRC and several
sections of the Atomic Energy Act allow the public to petition the NRC for specific
actions to provide safety for the general public.

The headlift of the TMI#2 reactor is a dangerous maneuver. This headlift is a
part of the claanup plan for the TMI#2 accident. The headlift will be scheduled
in the near futute according to correspondence between the NRC and the GPUNC.

Several questions were raised in the correspondence between the NRC and GPUNC
regarding pyrophoricity. Also comments were received from the public on the
dangers of pyrophoricity. (Letter Gulbransen , U of P to Snyder , NRC , dated
Aug.27,1930) I sent a letter to Mr Barrtet, NRC , dated July 25,1933. Mr Barrett
very kindly sent me an extensive reply which I have researched extensively. Although
I commend the researchers on their deligence in seeking out the facts, I also
take the researchers to task in that the conclusions   disagree
with the very facts that they report.

Basis of the request to stop headlift of TMI#2 reactor:

The pyrophoricity   of the zircalloy present in the TMI#2 reactor is still a
matter of conjecture. The research has not determined the full extent of the
pyrophoricity present in the #2 reactor.

The conclusions of the Evaluation of the Pyrophoric Issues Related to TMI@2
Underhead Characterization and Core Sampling by the NRC Chemical Engineering
Branch contradict the very facts upon which the conclusions are based:
A. "Bulk zirconium metal or zirconium hydride is normally protected from
reaction with air , water or hydrogen by a tight inpervious surface film of $ZrO2$."
This is not true,not proven at least,for zircalloy that has gone thru the temperature,
time and hydrodynamic stress hidtory of a TMI#2 accident. This NRC evaluation
must not bear   weight in this headligt operation.

B. "At high temperatures, zirconium hydrides react with steam to form ziconium oxide
and hydrogen gas."   This is not necessarily true if there is an excess of
hydrogen gas driving the reaction toward hydride production. An excess of
hydrogen would exist in the TMI#2 reactor during the accident if hydrogen gas
was being continually introduced during the accident. There is evidence that
hydrogen was being continually introduced during the accidant.
(1). There was an hydrogen bubble that was stable for several days.
(2.) There was an hydrogen "Spike."
(3.) The hydrogen mentioned in the Hartment allegations could and probably
was allowed to remain on providing a source of hydrogen during the accident.

C. "The inert diluents would help to dissapate reaction heat and prevent
the development of pyrophoric conditions." This statement of the NRC CEB
contradicts Page 4 of the Accident and Fire Prevention Information USAEC Issue 45
August 7,1983, which states,"The evidence suggests that trace contaminants in
zirconium may contribute to increased pyrophoricity."

There are many weaknesses in the NRC development of the danger of pyrophoricity in—

There are many weaknesses in the NRC development of the danger of pyrophoricity in the TMI#2 reactor. The above   are only a few of the most obvious.

I respectfully .   request that the headlift be postponed until a full public review of this issue can proceed.

Very truly yours,

M. I. LEWIS
6504 BRADFORD TERR.
PHILA., PA. 19149

University of Pittsburgh

SCHOOL OF ENGINEERING
Department of Metallurgical and Materials Engineering

November 1, 1983

Secretary
Nuclear Regulatory Commission (N.R.C.)
Washington, D.C.   20555

Dear Mr. Secretary:

   Mr. Marvin Lewis has asked me to send a copy of my letter to him in support of his objections to the removal of the reactor head of the damaged T.M.I. #2 reactor. Attached find my letter to Mr. Lewis dated September 28, 1983 together with a paper on the effects of oxygen, nitrogen and hydrogen on the mechanical properties of zirconium.

   I hope the NAC will exert the greatest caution before proceeding with lifting of the head of the reactor.

Very truly yours,

Earl A. Gulbransen
Research Professor

EAG:sj
Enclosure

cc: Mr. Marvin Lewis

839407

September 28, 1983

Mr. Marvin I. Lewis
6504 Bradford Terr.
Philadelphia, PA 19149

Dear Mr. Lewis:

I have your letter of September 13, 1983. I think you have made
some very strong points in your letter to the Nuclear Regulatory
Committion (NRC). One would normally assume that the NRC is aware of
the many hazards associated with removing the reactor head of the damaged
reactor. I would like to make a few comments on the facts developed in
your letter.

First, under A, zirconium is normally protected as is zirconium
hydride by a surface film of ZrO_2. This is certainly not true of the
Zircaloy which had gone through the temperature, stress and reaction
conditions during the accident. It is very hard to predict what the
present condition of the remaining Zircaloy and zirconium hydride is in
the reactor. Finely divided zirconium hydride may have spalled off of
the cladding and is still present as hydride in the bottom of the
reactor. In a finely divided state it could be very pyrophoric. The
reactor core must be kept under water at all times until it is proven that
Zircaloy and zirconium hydride are not present.

Second, under B, no data is available to decide whether zirconium
hydride, zirconium oxide or a mixture would form in the cladding under
the accident condition at TMI #2. We must assume the worst possible
conditions to avoid further dangerous events on exposing the core to air.

Third, under C, inert constituents in the Zircaloy may seriously
increase the pyrophoric properties. Thus, oxygen, nitrogen and hydrogen
amkes the Zircaloy very brittle and lead to fragmentation of the cladding
and to increased pyrophoricity.

I am enclosing a short survey on the effects of oxygen, nitrogen and
hydrogen on the mechanical properties of zirconium. I hope you will
find it of interest.

In conclusion it is essential to keep all operations on the damaged reactor under water at all times to avoid possible serious reactions of air with unreacted Zircaloy and zirconium hydride.

I was glad to receive your letter and to hear that you are concerned about possible future catastrophic events at TMI #2.

Very truly yours,

Earl A. Gulbransen
Research Professor

EAG:sj
Enclosure

The Effect of H, O and N Gases on the Mechanical
Properties of Zirconium and Zirconium Alloys

by
Earl A. Gulbransen
University of Pittsburgh, Pittsburgh, PA

1.1 Introduction

The mechanical properties of zirconium and zirconium alloys depend strongly on the H,O and N contents.[1,2] Zirconium has a strong affinity for all of the three gases in contrast to Fe and many other common metals. In the Fe-H system[3] where the affinity between the metal and hydrogen is small hydrogen dissolves endothermally and in small quantities. No compounds are formed yet hydrogen has a major effect on the mechanical properties. In the Zr-H system compounds are formed and the gas dissolves in the metal exothermally and in comparatively large quantities.

In the Zr-O and Zr-N systems very stable compounds are formed[4] and the gases dissolved in the metal exothermally and in large quantities.[1] Small quantities of all of these gases have a major effect on the mechanical properties of zirconium and zirconium alloys.[1,2]

1.2 The zirconium-hydrogen system

Figure 1 shows a phase diagram of the Zr-H system with isobars.[1] The diagram is of the eutectoid type. Zr undergoes a phase transformation at 862°C from the hexagonal close-packed to the body-centered cubic structure. The low temperature phase is called the α-phase and the higher temperature phase the β-phase. The maximum amount of hydrogen taken up corresponds to the composition $ZrH_{1.98}$.

The maximum solubility of hydrogen is referred to as the terminal solubility. The terminal solubility of hydrogen in the α-phase is smaller than in the β-phase. At the eutectoid temperature of 550°C the terminal solubility in α-Zr is about

6 atom % and in β-Zr about 37 atom %.

Three hydrides occur in the Zr-H system: the cubic δ-ZrH$_{1.4}$, the tetragonal ϵ-ZrH$_{1.98}$ with c/a < 1 and the tetragonal γ-ZrH with c/a > 1.[1] The γ-ZrH phase is only stable below 260°C. Both the δ and the ϵ hydride phases have extensive ranges of homogeneity.

From the phase diagram, Figure 1, the terminal solubility of hydrogen in both α and β Zr increases with increase of temperature. Dissolution of the hydride takes place into the saturated solution of hydrogen in Zr endothermally. Figure 2 shows the terminal solubility of H in α-Zr in parts per million as a function of 1/T.[1] At a PWR nuclear reactor operating temperature of 350°C a terminal solubility of 120 ppm is found.

1.3 Embrittlement of zirconium by hydrogen

Hydrogen is a very dangerous impurity in zirconium and zirconium alloys. Hydrogen can be absorbed in these metals by corrosion in high temperature water and steam.[2] Due to the decrease in the terminal solubility with decreasing temperature, the hydrogen content of the metal is greater than the metal can hold in saturated solution at room gemperature. As a result hydrogen contents of a few tens of ppm or more are sufficient to cause embrittlement.[2]

When the excess of hydrogen before testing is present as hydride impact embrittlement is observed. This becomes more severe with increase of strain rate and at decreased temperatures. If the excess of hydrogen before testing is present as a supersaturated solution in the metal, low strain rate embrittlement occurs. Low strain rate embrittlement depends on the rejection of hydrogen from the supersaturated solution during plastic deformation. This occurs by the precipitation of a crystalline brittle δ-ZrH$_{1.4}$.

For pure zirconium there are indications that significant supersaturation with hydrogen never occurs.[2] Even after rapid cooling the hydride is probably present as fine particles of δ-ZrH$_{1.4}$ which tend to coalesce with time. When

the metal is cooled slowly the hydride precipitates in the form of platelets
which lie parallel to the crystallographic planes of the {1010} type, i.e.
parallel to the principal slip planes in zirconium.

For alloys of zirconium supersaturation with hydrogen can occur causing low
strain rate embrittlement.

Figure 3 shows the influence of H on the ultimate tensile strength ϵ_B, the
% elongation δ and the % reduction in area Ψ when Zr is subject to plastic
deformation at room temperature.[1] The decrease in % elongation on fracture
and the decrease in % reduction in area on fracture are indicators of embrittle-
ment of the metal. Figure 3 shows a H content of 100 ppm has decreased the %
elongation by a factor of 3. The same factor of 3 is found for the decrease in
the % reduction in area. In contrast the ultimate strength is not seriously
effected by 100 ppm of H. We conclude that 100 ppm can cause severe embrittle-
ment of zirconium at room temperature.

1.4 The zirconium-oxygen system

Zirconium reacts with oxygen, air, water and steam to form an oxide ZrO_2
with the oxide dissolving slowly into the metal especially at the grain boundaries
of the metal. The rapid dissolution of oxygen into the metal at the grain
boundaries has been reported in France in 1974[5] at temperatures below 650°C.

Figure 4 shows a phase diagram for the Zr-O system with isobars.[1] Only
one major oxide ZrO_2 is formed.[5] Below 1000°C the structure is monoclinic,
above tetragonal. At very high temperature the structure becomes cubic.[1]
Below ZrO_2 a number of suboxides have been observed Zr_8O, $Zr_{5.6}O$, $Zr_{3.7}O$, $Zr_{3.1}O$,
$Zr_{2.9}O$, $Zr_{2.7}O$ and Zr_2O with the hexagonal structure and ZrO with the cubic
structure.[1] The terminal solubility in the α-Zr phase is shown as about 30 atom %
below 1200°C. The terminal solubility in the β-Zr phase is much smaller. At
1200°C it is about 3.3 atom %.

Figure 5 shows the terminal solubility of O in β-Zr in atom % as a function of temperature.[1] The solubility increases with increase of temperature indicating an endothermic solution of oxygen from the α to the β phases of Zr. The transition temperature for α-β Zr increases with the oxygen content of the Zr.

1.5 The embrittlement of zirconium by oxygen

Figure 6 shows the influence of O on the ultimate tensile strength δ_B, the yield strength $\delta_{0.2}$ and % elongation δ at room temperature.[1] For an O content of 0.1 wt % (1000 ppm) the ultimate tensile strength δ_B and yield strength $\delta_{0.2}$ are greatly improved. However, the % elongation is decreased by a factor of 2 which indicates embrittlement of the zirconium. The addition of 1000 ppm of oxygen to zirconium has a serious deleterious effect on the mechanical properties of Zr.

1.6 The zirconium-nitrogen system

Figure 7 shows a phase diagram for the Zr-N system with isobars.[1] Only one nitride ZrN with the cubic structure has been observed. The terminal solubility in α-Zr is shown as about 20 atom % at room temperature and 23.5 atom % at 1200°C. The terminal solubility in the β-Zr phase is much smaller. At 1200°C it is about 1.3 atom %.

Figure 5 shows the terminal solubility of N in β-Zr in atom % as a function of temperature.[1] The solubility increases with increase of temperature indicating an endothermic solution of nitrogen from the α to the β phases of Zr. The transition temperature for α-β Zr increases with the nitrogen content of the Zr.

1.7 The embrittlement of zirconium by nitrogen

Figure 8 shows the influence of N on the ultimate tensile strength δ_B, the yield strength $\delta_{0.2}$ and the % elongation δ at room temperature.[1] For an

nitrogen content of 0.1 wt. % (1000 ppm) the ultimate tensile strength δ_B and the yield strength $\delta_{0.2}$ are improved by a factor of 5. However, the % elongation is decreased by a factor of 5 which indicates severe embrittlement of the zirconium. The addition of 1000 ppm of nitrogen has a serious deleterious effect on the mechanical properties of the zirconium.

J. Gulbransen

11/1/83

2.1 List of figures

1. Zr-H Systems with Isobars

2. Terminal Solubility H in Zr ppm

3. Influence of H on Ultimate Strength, % Elongation and % Reduction in Area of Zr at Room Temperature

4. Zr-O System with Isobars

5. Terminal Solubilities for H, N, O and C in Zr

6. Influence of O on Ultimate Strength, Yield Strength and % Elongation of Zr at Room Temperature

7. Zr-N System with Isobars

8. Influence of N on Ultimate Strength, Yield Strength and % Elongation of Zr at Room Temperature

3.1 List of references

1. E. Fromm and E. Gebhardt book "Gase und Kohlenstoff in Metallen", Springer-Verlag, Berlin 1976, p. 419-430.

2. J. O. Fast book "Interaction of Metals and Gases Vol. 1 Thermodynamics and Phase Relations", Academic Press, New York 1965, p. 175, 179, 197, 198.

3. Reference 2, p. 126-148.

4. JANAF Thermochemical Tables, Second Edition NSRDS, NBS 37, U. S. Government Printing Office, Washington, DC 1971.

5. J. L. Lereddi, G. Berenger, C. Roguqes - Carmes and P. Lacombe 25e Reunion Internationale Societe de Chimie Physique Dijon Juillet 8-12, 1974.
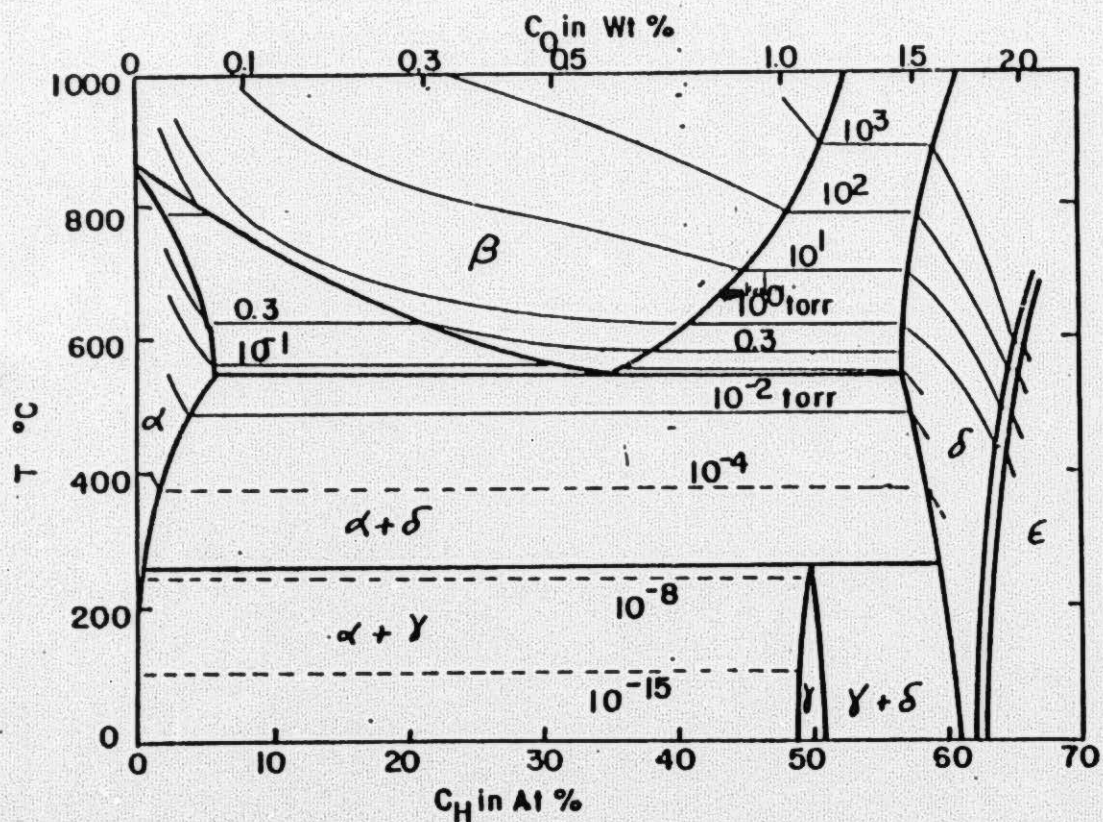
Fig. 1   Zr-H System with Isobars   (Fromm and Gebhardt   Gase und Kohlenstoff
in Metallen   Springer-Verlag Berlin   1976   p. 426)
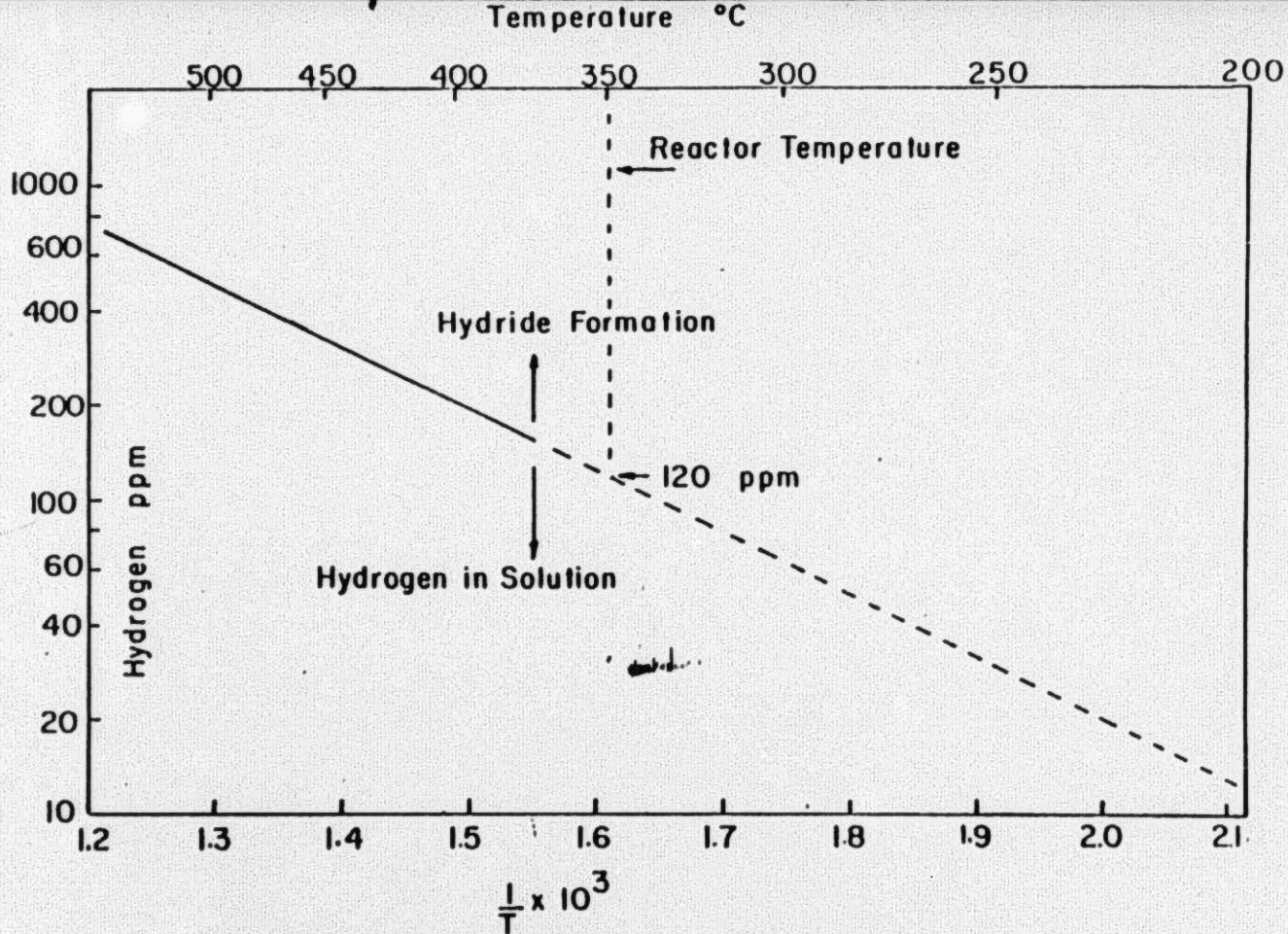
Fig. 2 Terminal Solubility H in Zr ppm (Gulbransen & Andrew)
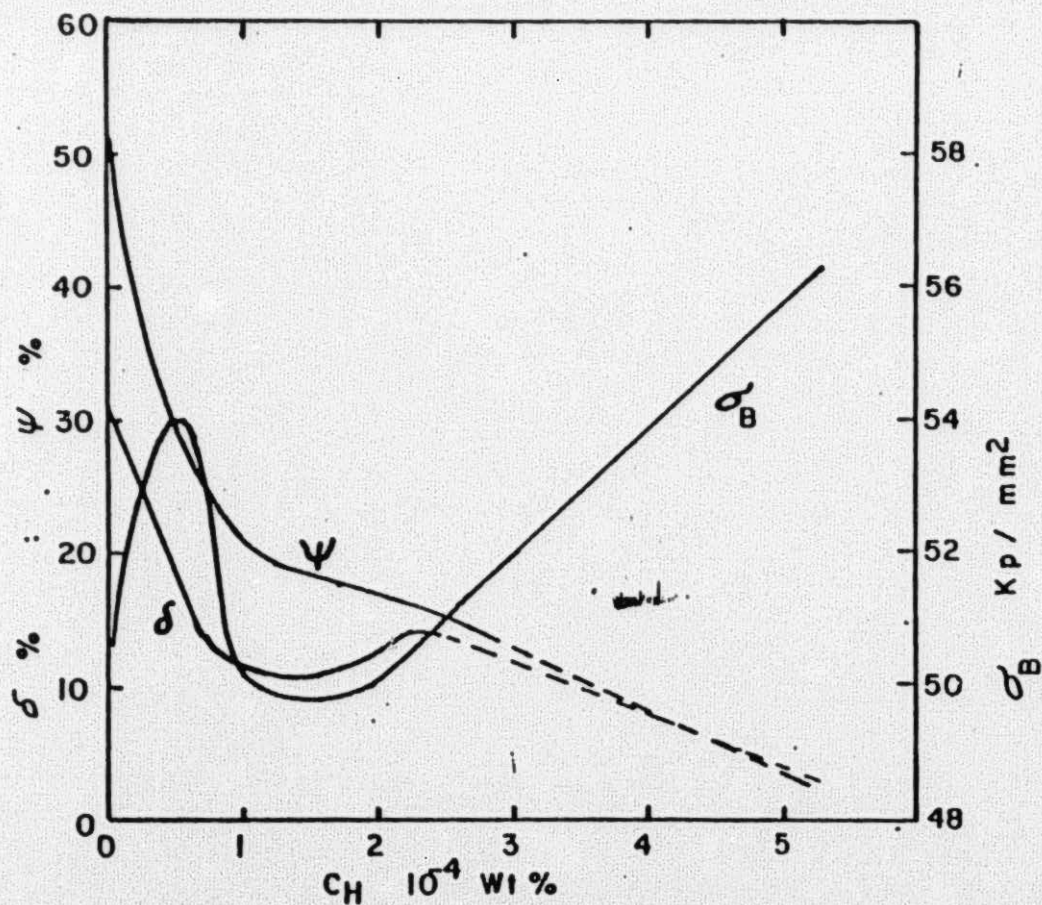
Fig. 3 Influence of H on the Ultimate Tensile Strength σ_B , the % Elongation δ and the % Reduction in Area Ψ of Zr at Room Temperature. (Fromm a Gebhardt Gase und Kohlenstoff in Metallen Springer Verlag Berlin 1976 p 427
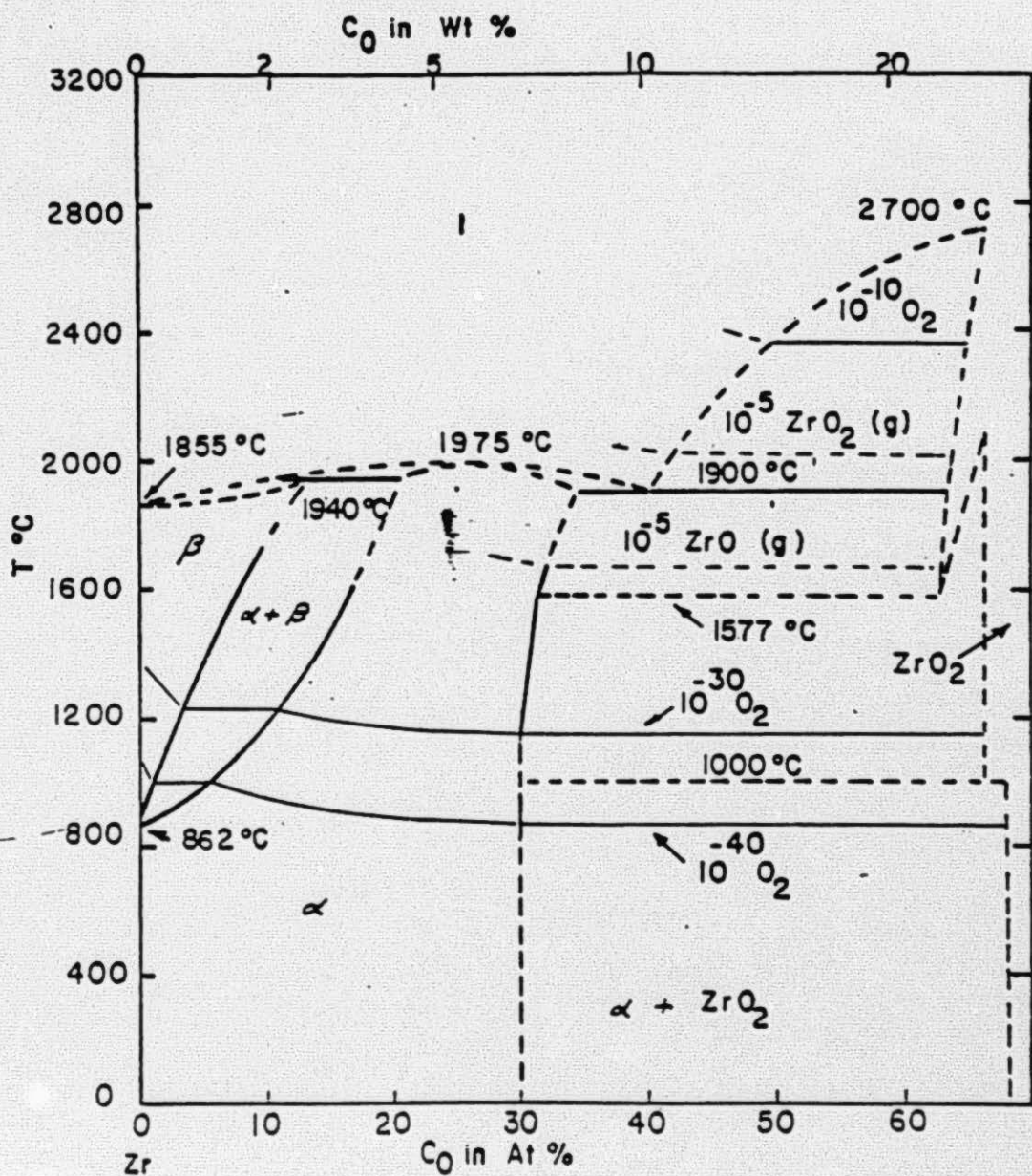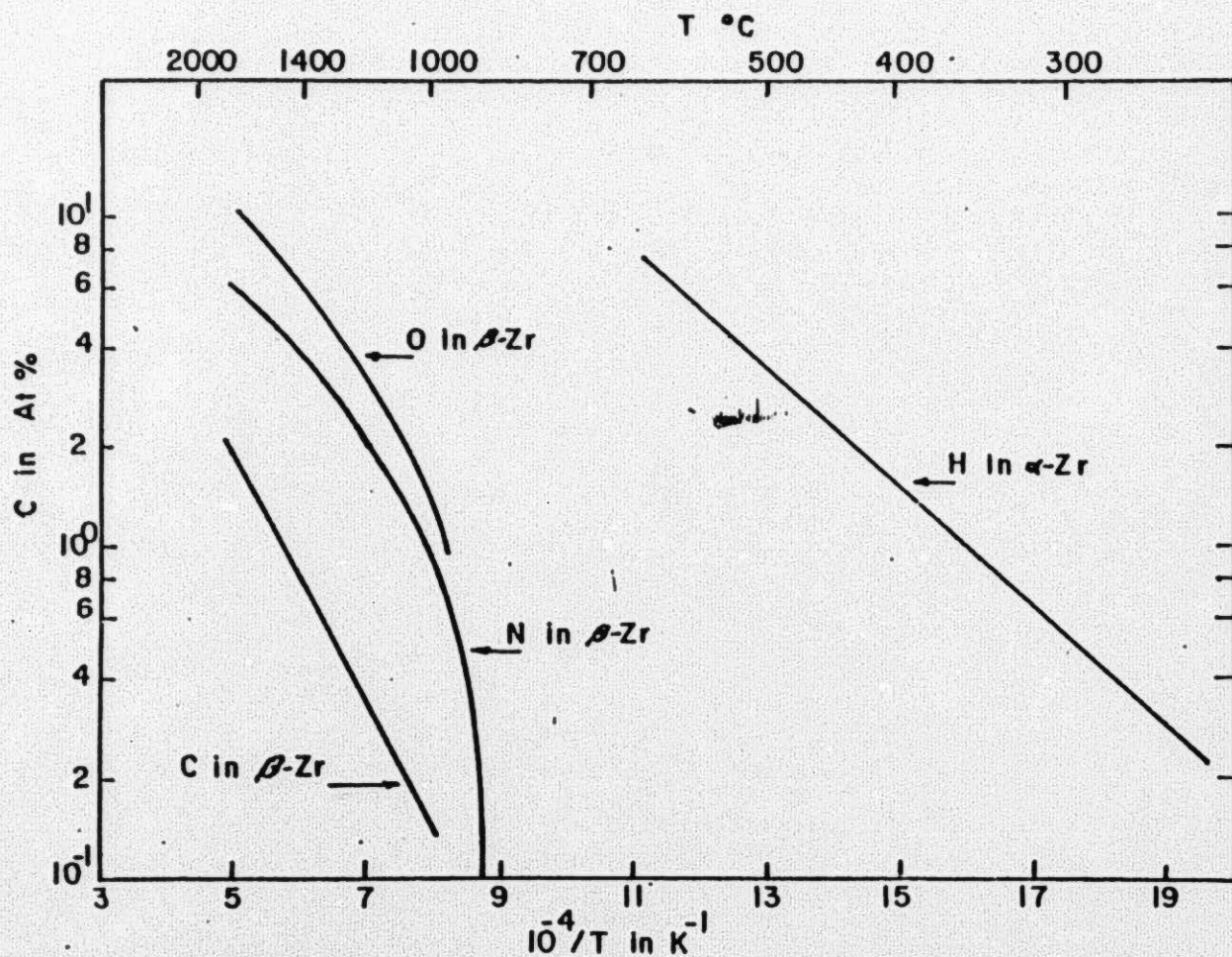
Fig. 4 Zr-O System with Isobars (Fromm and Gebhardt Gase und Kohlenstoff in Metallen Springer-Verlag Berlin 1976 p.426)

Fig. 5 Terminal Solubilities for H, N, O & C in Zr (Fromm and Gebhardt Gase und Kohlenstoff in Metallen Springer- Verlag Berlin 1976 p.427)
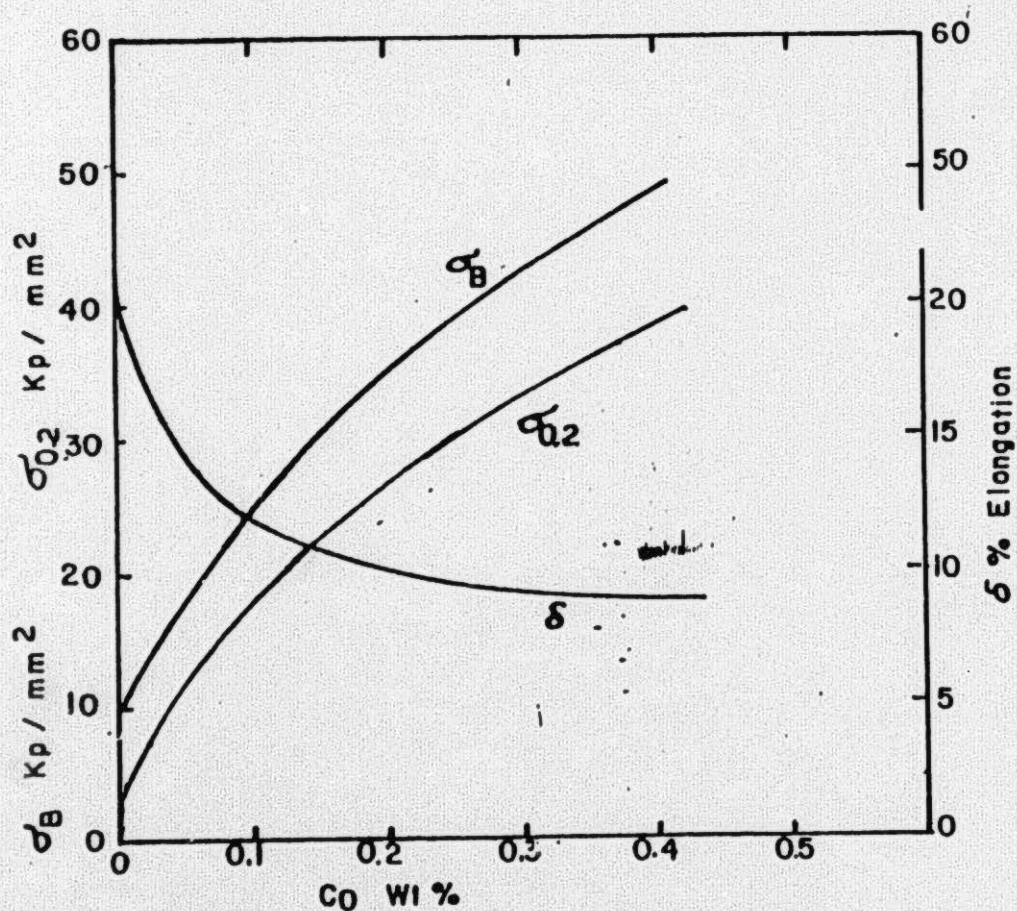
Fig. 6 Influence of O on Ultimate Tensile Strength σ_B, Yield Strength $\sigma_{0.2}$ and % Elongation δ at Room Temperature
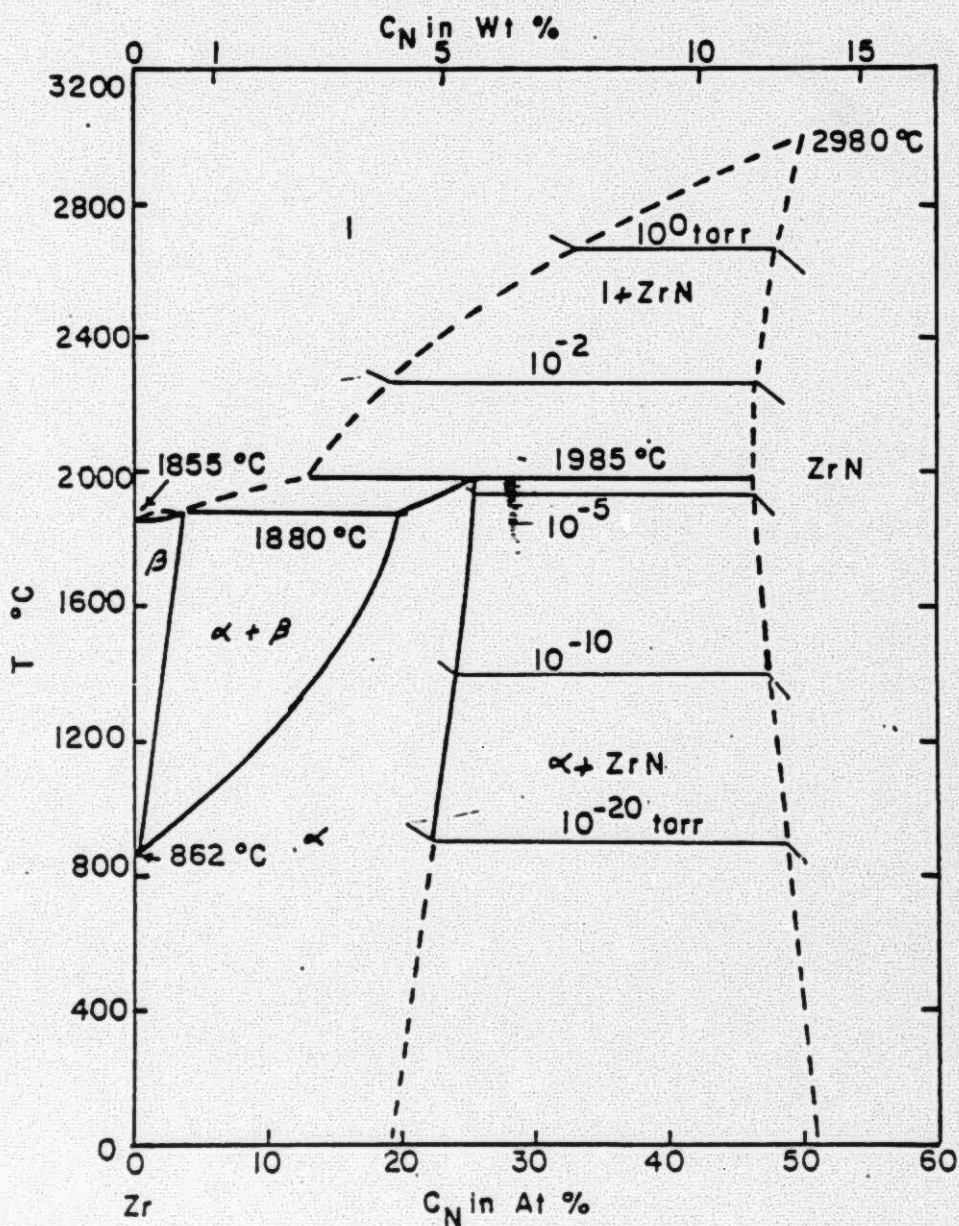(Fromm & Gebhardt Gase und Kohlenstoff in Metallen Springer Verlag Berlin 1976 p 430

Fig. 7 Zr-N System with Isobars (Fromm and Gebhardt
Gase und Kohlenstoff in Metallen Springer-Verlag Berlin
1976 p.428)

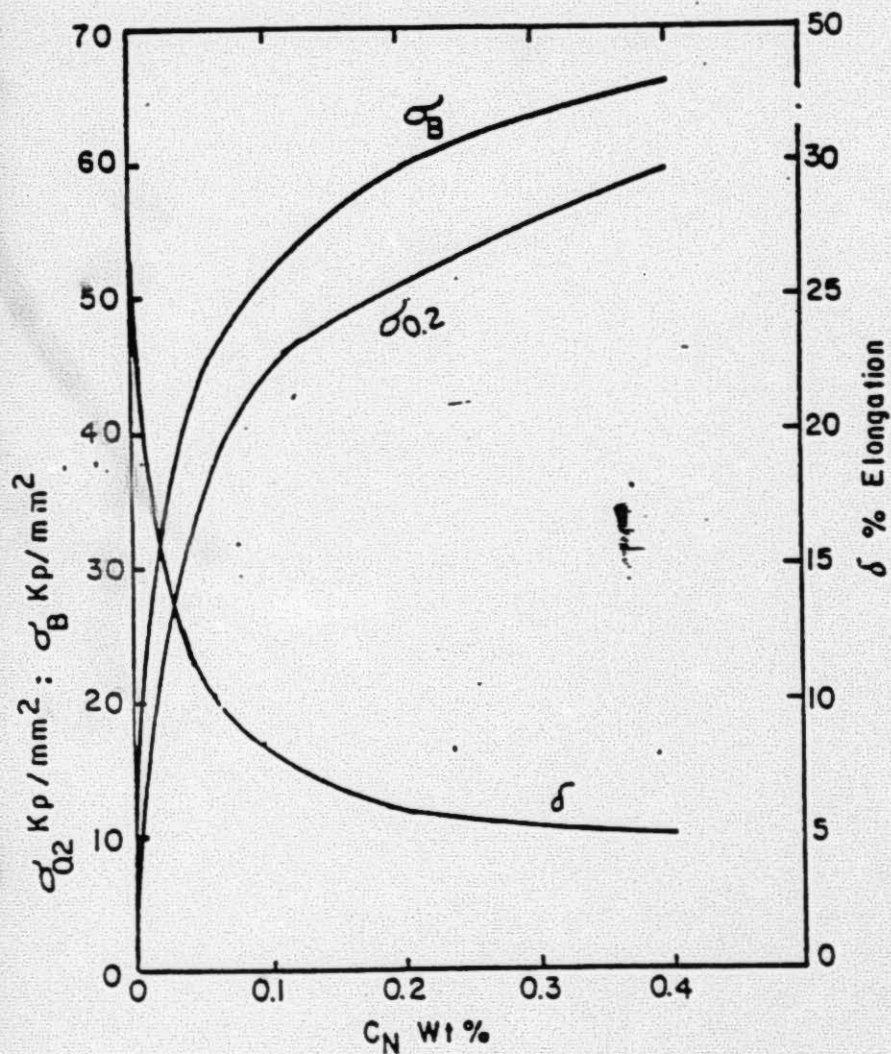Fig. 8 Influence of N on Ultimate Tensile Strength σ_B,
Yield Strength $\sigma_{0.2}$, and the % Elongation δ of Zr at Room
Temperature. (Fromm & Gebhardt Gase und Kohlenstoff in Metallen
Springer Verlag Berlin 1976 p 428)