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Gen. Electric Co.
IRRADIATION PROCESSING DEPARTMENTSeptember 29, 1960
+ the
DECRECENT ZIRCONIUM FIRE EXPERIENCE AT HANFORD
AND THE GENERAL ZIRCONIUM FIRE PROBLEM

by

G. E. Zima

INTRODUCTION

Under certain metal and environmental conditions, zirconium and zirconium-base alloys can present a fire and explosion hazard. The potential large scale application of Zr-2 to Hanford reactors forces attention to this characteristic of zirconium alloys. It is the intent of this report to review the recent fire experience in the course of process tube installation at C-Reactor and to give a brief appraisal of the general Zr-2 fire situation at Hanford reactors.

SUMMARY

1. Test work to-date has indicated that ignition and propagation of ignition in massive Zr-2 components, such as process tubes, is extremely improbable under conceivable environmental conditions presented by Hanford reactors. Small particles of Zr-2 are readily ignited. The fire and explosion hazard increases with the quantity of finely divided material allowed to accumulate.
2. Close inventory must be kept on wastes from machining operations. Large accumulations of Zr-2 fines should not be permitted to develop in working or disposal areas. Particular care should be exercised around operations, such as sawing, which generate powdered Zr-2. Incineration is believed to be the best method of disposing of waste Zr-2.
3. Fires involving small aggregates of Zr-2 fines can be extinguished by water, preferably applied in a spray. The control of fires involving a large quantity of Zr-2 fines can be a difficult, and hazardous, undertaking. Reasonable housekeeping and disposal precautions can prevent such a situation at Hanford reactor sites.

RECENT ZIRCONIUM FIRE EXPERIENCE AT HANFORD

Certain machining operations must be performed on as-received Zr-2 process tubes prior to final installation in the reactor. Recently, minor fires have been experienced in the course of this work. The following is submitted in description of these incidents.

Prior to the actual Van Stoning operation, the process tube sections are cut to the proper length by an air-driven cutter, which couples to the gunbarrel flange--or a facsimile. Roughly 1/4 inch of tube length is removed by the cutting. This generates a quantity of turnings. The thickness of the turnings depending on the cutting speed. A water-soluble oil is applied by a hand held nozzle and an attempt is made to distribute the fluid uniformly over the cutting zone. One such cutting operation is performed before installation in the reactor and the second cutting is, necessarily, made on the installed tube. The incidents in question occurred during the second cutting on the rear face of C-Reactor.

In the first fire instance, a small ball of turnings located in the cutter housing ignited. The fire was quenched immediately upon application of water. In the second instance, a similar quantity of turnings (about equivalent in volume to a 1-1/2 inch diameter ball) ignited in the cutter housing. Application of water in the second case failed to quench the fire and the cluster of chips burned completely. Access to the fire zone was apparently poor in this case, preventing efficient use of the water.

The temperature of the cuttings is largely determined by the cutting speed and the cooling ability of the cutting oil. Apparently there is considerable variation in both of these factors from one tube operation to the next. The low incidence of fires (2 in over 50 tube installations) suggests that reduction of cutting speed and more generous application of cutting oil, would make a fire event during this operation highly improbable. In neither of the cases cited above was there a suggestion that massive zirconium, i.e., the uncut tubing, was involved in the fire action. Examination of similar turnings from the cutting operation showed that the sensitive material varied in thickness from roughly a few mils to about 1/16 inch, with a width of the order of 1/8 inch, or smaller. Single strands of this material could be ignited by a match, but the burning stopped after withdrawing the heat source. Aggregates of the turnings continued to burn after removing the match. This material, however, appeared to be considerably less inflammable than magnesium in a similar state.

There have been other, minor, instances of pyrophoric display during the machining operations incidental to process tube installation. In addition to the cutting operation noted above, the as-received tubes are sawed to a working length prior to the Van Stoning operation. Sawing generates Zr-2 fines which spark occasionally. Judging from the single sawing operation witnessed, there appeared to be less sparking from Zr-2 than from a ferrous base metal.

Fire Probability and Current Countermeasures

Control of machining wastes appears to be reasonably good. The design of the cutter, discussed above, is such that most of the cuttings are retained within the cutter housing. The cutter is carefully cleaned of zirconium-waste after each cutting operation is completed. Cuttings are consigned to a water-filled bucket immediately and so held until burial. With present equipment and procedures, there appears to be little likelihood of depositing a significant quantity of Zr-2 waste in the rear-face hardware. Present practice calls for burying the scrap as soon as practicable after the machining operations. Each accumulation is buried separately to avoid the formation of large aggregations of scrap in the disposal area.

Other than the machining operations attending tube installation, there appears to be little opportunity to degrade the Zr-2 of the process tubes to a potentially pyrophoric form during the ex-reactor residence of the tubes at Hanford. Storage of the tubes should pose no problems in this respect. There is virtually no possibility of generating a dangerous quantity of fines by storage or occasional tube-tube contact during storage. Ignition, and propagation of ignition, in a system of massive Zr-2 components would require continuous application of an intense heat source over a substantial portion of the Zr-2 involved, together with a copious and continuous supply of oxygen to the burning zone. These conditions would appear virtually impossible of attainment in the storage and service environments of the Zr-2 process tubes. Storage facilities designed to preserve the surface integrity of the tubes, i.e., a system which prevents tube-tube contact and contact with abrasive materials in general, should also prevent a dangerous accumulation of fines derived from the tubes.

The process of removing veteran process tubes from the reactor could generate some chips and fines--some of which would be deposited in the graphite. Under normal stack atmosphere conditions these Zr-2 particles should present no problem. With a substantial air incursion to the stack, these Zr-2 particles could ignite and, possibly, aggravate the graphite oxidation situation. Under such conditions, however, zirconium ignition would doubtless be regarded as one of the lesser problems. Cracks developed in the tube by severe mechanical action on the tubes during tube removal operations would increase the tube area available for reaction. Without a severe tube temperature excursion, accompanied by a strong oxidizing atmosphere, this cracking probably would not significantly increase the fire hazard of the Zr-2 tubes.

The influence of irradiation on the pyrophoric characteristics of Zr-2 is not known to any extent. It is expected, however, that irradiation would not significantly change the ability of massive Zr-2 to resist fire action.

General Remarks on Zirconium Pyrophoricity

A brief summary of the status of present knowledge on zirconium pyrophoricity is appropriate to this report.

- A. Without exception, serious explosions and fires experienced with solid zirconium have involved aggregates of small particles--powder, chips, etc.--and mixtures wherein a substantial portion of the total mass was comprised of small particles.
- B. The specific area (surface area/mass of particle) has been established as a controlling factor in the ignition and propagation of ignition in zirconium. Work at Argonne⁽¹⁾ has shown that there is a roughly linear relationship between the logarithm of the ignition temperature (lowest temperature at which combustion can be self-sustained) and the logarithm of the specific area--the ignition temperature decreasing with increasing specific area. Attempts to relate such factors as specific area, activation energy for oxidation, and ignition temperature have been fairly successful. Some interesting data from reference 1, derived from theory and experiment, are given in Table I. An attempt is made here to indicate the relative pyrophoricity of a number of metals, in bulk and finely divided form. It is interesting to note that solid zirconium is regarded as substantially less pyrophoric than several other metals, such as molybdenum and vanadium which do not usually enjoy publicity in this respect. The pre-eminent position of uranium in this Argonne classification is noteworthy. The ignition temperature data of Table I are to be regarded only as rough, relative values for the indicated states of subdivision and not as absolute indices of the dangerous temperature levels for these materials. The latter are determined by a multitude of physical and chemical factors of the working environment which determine the heat generation and heat dissipation characteristics of the reacting system.

1. Schnitzlein, J. G., et al, "Metal Oxidation and Ignition Kinetics and Metal-Water Reactions;" ANL-RCV-SL-1657; 1960.

TABLE I

CALCULATED IGNITION TEMPERATURES OF VARIOUS METALS IN
BULK AND FOIL FORMS (Ref. 1)

Bulk Metal (Specific Area = 1 sq cm/g)		Metal Foil (Specific Area = 1000 sq cm/g)	
<u>Metal</u>	<u>Ignition Temperature (C)</u>	<u>Metal</u>	<u>Ignition Temperature (C)</u>
↑ U	527	↑ U	246
Mg	615	Nb	401
V	825	V	468
Mo	890	Mo	542
<u>Zr</u>	973	Ta	558
Fe	1119	Fe	576
Ta	1135	Th	588
Ti	1322	Mg	615
Cu	1392 (p.m.p.)	<u>Zr</u>	623
Th	1567	Cu	771
Nb	∞	Ti	822

Increasing Pyrophoricity

Increasing Pyrophoricity

Argonne work⁽¹⁾ has also shown that the propagation of combustion is closely related to the specific area factor. For a given specimen length and width, the burning propagation rate has exhibited a nearly linear dependence on the thickness in a log-log plot, the propagating rate increasing with decreasing thickness. For a given thickness, zirconium ranks relatively high in propagation ability.

Both ignition temperature and burning propagation data have shown that ignition and fire destruction of massive zirconium components are extremely improbable events under atmosphere and temperature conditions which could, conceivably, obtain during reactor accident conditions.

- C. Water and water vapor are known to have a potent influence on the pyrophoric behavior of zirconium, although the nature of this influence remains obscure. In virtually every recorded instance of major fire, or explosion, action involving zirconium, water, in some quantity, is known to have been involved at some stage of the accident history. Hydrogen evolution accompanies a Zr-H₂O reaction and undoubtedly H₂ in free or hydride form--participates in fire or explosion events involving moist zirconium aggregates. There is some evidence that zirconium powder--H₂O mixtures containing roughly 5 to 15 percent H₂O, by volume, yield the maximum energy release upon suitable activation in shock sensitivity equipment.⁽²⁾ Small aggregates of zirconium fines covered with water should be indefinitely stable. A large aggregate, however, although completely immersed in water could present a serious fire, or explosion, hazard. Water seeping into such a mass could create a pyrophorically sensitive zone within the core of the aggregate which, upon suitable activation, could ignite with explosive violence. Piles of uranium machining wastes, immersed under twelve feet of water, have exhibited such a phenomenon. The properties of zirconium do not disqualify zirconium for a similar performance.
- D. Certain surface films generated by the reaction of zirconium with various gases, such as: O₂, CO₂, N₂, H₂ and H₂O, have exhibited a tendency to pyrophoric behavior, i.e., sparking when scratched, but no fire propagation.⁽²⁾ While this phenomenon may be significant to the ignition characteristics of aggregates of particles--possibly providing the trigger action--it would not be expected to markedly change the fire situation with respect to massive zirconium components.
- E. Zr-2 wires (50 to 100 mil diameter) have demonstrated ignition and propagation ability in steam-oxygen mixtures.⁽³⁾ These tests were conducted under high total pressures (900-2000 psi), and high oxygen partial pressures (60-1000 psi). The Aerojet work suggests that, for Zr-2, an oxygen concentration of the order of three volume percent in steam may be critical with

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2. Herickes, J. A., et al, "Zirconium Hazards Research," TID-5749, June 1958.
3. Higgins, H. M., "The Reaction of Zr-2 With Water and With Uranyl Sulfate Fuel Solutions," AGC-AE-40, March, 1958.

respect to ignition propagation of high specific area material. The data on gas pressure and composition effects are, however, very sparse. Stanford Research Institute (SRI) work, cited in reference 3, has shown that zirconium foil tensile specimens (12 mil thick x 0.5 inch wide) can ignite and burn to completion when broken under high pressure oxygen (approximately 1000 psi) at room temperature. Both the Aerojet and SRI work has shown that, under high pressure O_2-H_2O atmospheres, burning of foil and wire specimens, partially immersed in water, could propagate into the water bath to some extent. The atmospheres employed in these tests, while possibly somewhat realistic from the standpoint of pressure, represent a substantial departure, composition-wise, from atmospheres which could reasonably be expected to obtain in a reactor accident, or in the ex-reactor storage environment. Generally, these studies are further corroboration of the fact that the hazard potential of solid zirconium becomes increasingly important as the surface area/mass ratio of the metal increases. As noted above, the environmental conditions and state of aggragation of the discrete masses of zirconium are additional factors which determine the history of a pyrophoric event. Any specification of a "critical" specific area must be conditioned by these other factors.

- F. The utility of various fire quenching media depends on the fire circumstances. Fires involving small aggregates of chips, etc., can be readily quenched by water, preferably directed in a spray. Fires involving large masses of fines present a serious quenching problem. Recent work by Argonne⁴⁾ has shown that halogenated hydrocarbons (CH_2BrCl and CH_2F_2Cl (Freon-22)) are effective in quenching a zirconium fire. A concentration of roughly five volume percent of these agents in air has proved capable of stopping the propagation of ignition in zirconium foil. The possibility of generating toxic gases when using these halogen compounds demands that their use be restricted to well ventilated areas. The ability of these agents to handle a large fire involving zirconium fines is probably quite limited.

Powdered, inert, materials, such as dolomite, have proved effective in controlling--but not quenching--powder fires. At the high temperatures developed by ignition, zirconium will react readily with N_2 and CO_2 , so that application of these gases could possible aggravate the fire situation. The severely limited ability of known fire fighting techniques to cope with zirconium fires involving large masses of zirconium fines makes mandatory housekeeping, and inventory, practice which precludes such a situation.

RECOMMENDATIONS

Many aspects of the pyrophoric behavior of zirconium and Zr-2 remain obscure--a situation which forbids much generalization. Experience with zirconium, and other metals of comparable chemical reactivity, has, however, suggested some guides to minimizing the fire potential associated with the use of Zr-2 in Hanford reactors:

1. As with any potentially pyrophoric material, it is prudent to minimize close contact of Zr-2 with combustibles, i.e., to reduce, as far as is practicable, the heat producing potential of the environment--particularly in the immediate neighborhood of machining operations.
2. Close inventory should be maintained over zirconium waste generated by machining operations. Waste should be placed under water as soon as a convenient break in the machining operations permit. Special care should be exercised around saws, which generate powdered Zr-2. Large accumulations of powder are to be avoided. If direct fall into a water bath from the machine is not practical, powder should be carefully transported to a temporary storage container by a non-sparking tool. Open metal containers should be used for temporary storage of Zr-2 waste. The quantity of waste per container should be limited to several pounds, or less. Containers should be taken to the disposal area as soon as convenient. Disposal of zirconium fines by incineration is preferable to burying. Disposal of irradiated Zr-2 process tubes is probably best done by burying according to current Hanford practice.
3. No housekeeping, or fire prevention program, can anticipate all the situations which might develop in the course of large scale application of Zr-2 to Hanford reactors. The fire potential of zirconium demands that there be clear-cut responsibility for the exercise of prescribed practice for handling zirconium and for the periodic review of this practice for adequacy.

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