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AN EVALUATION OF THE ZIRCONIUM HAZARD

BY

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AUGUST 14, 1956

HANFORD ATOMIC PRODUCTS OPERATION

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Chemistry
(TID-4500, 11th Ed.)

AN EVALUATION OF THE
ZIRCONIUM HAZARD

By

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Heavy Element Chemistry Unit
Separations Technology Section

August 15, 1956

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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AN EVALUATION OF THE ZIRCONIUM HAZARD

W. R. DeHollander

INTRODUCTION

On May 14, 1956, at Oak Ridge, Tennessee, two men were killed and a third maimed for life when a drum containing zirconium metal powder scrap exploded.⁽¹⁾

On April 28, 1955, 159,000 pounds of zirconium scrap were destroyed in a fire of unknown origin.⁽²⁾

The above described incidents are but two of more than thirty minor and major incidents involving some form of zirconium metal. In the light of such major incidents as the above, it is wise to review what is known about zirconium and the hazards attendant upon its use. Perhaps by re-emphasizing the hazardous and non-hazardous aspects of the zirconium picture, work with this metal may resume without trepidation.

OBJECTIVE

The objective of this study was to review the extensive literature on metallic zirconium in order to determine and evaluate the knowledge available concerning its hazardous nature.

SUMMARY AND CONCLUSIONS

The hazard of zirconium exists primarily in metal shapes of high surface to mass ratio. The primary sources of hazardous material are flash powder, discarded reduction residues from the Kroll process, poor grade sponge from the Kroll process, incompletely reacted sponge in the iodide process, and dirty, oily fine scrap. Massive metal in sizes as fine as sawdust is not hazardous when properly stored. Clean, dry, cool storage is preferred to storage under water and storage on sand beds is preferred to storage in concrete bays. Oily scrap hazard is due primarily to the ignition of the oil residue which can possibly ignite the metal. Zirconium does not represent a new kind of hazard but instead the difference

between zirconium and other combustible materials such as iron, uranium, copper, flour, sawdust, coal, oily rags, magnesium, and even rats nests is one of degree only.

REVIEW OF THE LITERATURE

As long ago as 1825, Berzelius⁽³⁾ was well aware of the explosive hazard of zirconium. He mentions that explosions resulted when zirconium metal (impure and finely divided, as was all zirconium, at that time) was heated with hydrated borax, alkali hydroxides, zirconium hydroxide, copper oxide, or lead oxide.

Later investigators were not able to reproduce some of these experiments using pure zirconium but many of them were repeated.

Berzelius also mentions a pyrophoric compound, ZrOS, made by heating zirconium sulfate to 380° - 400° C in hydrogen sulfide then cooling in hydrogen sulfide.

Wedekind, as reported in Mellor⁽⁴⁾ mentions that zirconium made by reducing potassium zirconium fluoride with potassium under air-free conditions ignited spontaneously after 14 hours exposure to air.

Chambers⁽⁵⁾ in 1933 describes in detail several incendiary and primer compositions, evidencing the fact that zirconium was chosen for its sensitivity and explosive nature. He also mentions that ignition tests are a good method of checking metal uniformity. Metal powders with ignition temperatures of 210° C were preferred and could be controlled to within $\pm 5^{\circ}$ C. The dependence of ignition temperature on grain size is also mentioned. Compositions of zirconium powder with barium nitrate or potassium chlorate or lead peroxide could be ignited by the impact of an 8 ounce steel ball dropped 15 inches. It is evident that the explosive property was appreciated since these compositions were compared favorably with mercury fulminate.

Hart and Tomlinson⁽⁶⁾ in 1951 published a table of the various metals and their usefulness as additives to modern explosives and incendiaries to

increase their effectiveness. Zirconium is credited with an adiabatic temperature of oxidation of 14,300 C compared with aluminum at 13,300 C and magnesium at 12,200 C. Again the sensitivity of these finely divided metals is emphasized.

Kopelman and Compton⁽⁷⁾ mention 80 articles concerning the spontaneous ignition of metal powders in the past forty years and point out that an appreciable number of fires and burns still result from this cause. They state that uranium is so much more reactive than zirconium that, whereas zirconium powder is usually stored under water, uranium powder of the same particle size will catch fire under boiling water.

The variation in reactivity, and thus of pyrophoric nature of the various oxidizable metals is one of degree rather than kind. With the exception of the noble metals, platinum, gold and so on, all the common metals oxidize in air. Under the proper conditions they may burn and even undergo spontaneous ignition. For example; iron, copper and nickel 0.01 - 0.03 microns in particle size, tungsten 1 micron in particle size and zirconium and sodium 10 microns in particle size will all spontaneously ignite in air on disturbance or light impact.

Hartman, Nagy and Jacobsen⁽⁸⁾ studied the explosive properties of titanium, zirconium, thorium, uranium and their hydrides. Zirconium was the most sensitive to electrical ignition by sparks and had a higher relative inflammability. Dust clouds of uranium, uranium hydride and zirconium ignited at room temperature immediately upon dispersion.

Throughout the unclassified literature there are many examples of spontaneous ignition of metal powder but only a few instances of the spontaneous ignition of massive metal, notably uranium and magnesium. In those instances where fire occurred in massive metal, generally very heavy cutting forces were used, and ignition was brought about by a hot chip falling into a pile of finer turnings.

It can be assumed that there is ample knowledge concerning zirconium and its explosive characteristics. Most of the recorded incidents can be

explained and could have been predicted a priori from known data.

The ignition temperature of oxidizable materials is so dependent on the surface to mass ratio (i.e. particle size) and mass of sample that this feature is analyzed at length in the next section.

DEPENDENCE OF IGNITION TEMPERATURE ON PARTICLE SURFACE AREA AND MASS OF SAMPLE

Perhaps the most reliable source of data on the combustion of zirconium powders is the work of Andersen and Belz⁽⁹⁾ at Foote Mineral and Hartman, Nagy and Jacobsen⁽⁸⁾ at the Bureau of Mines. Their experiments have illustrated the dependence of ignition temperature on average particle size or surface area per gram. In zirconium powders, the surface area in square meters per gram is within 10% of the reciprocal of the average particle size in microns. The various available data on ignition temperature and particle size are tabulated in Table I and plotted in Fig. 1. Figure 1 is a plot of surface area in square meters per gram or the reciprocal of the average particle size in microns as a function of the reciprocal absolute ignition temperature. Such a plot was chosen on the basis of the work of Andersen and Belz.

Essentially what these authors have done is to utilize known rates of oxidation for zirconium and to make some assumption concerning the rate of heat loss to arrive at an expression for the ignition temperature.

FIGURE 1
IGNITION TEMPERATURE OF ZIRCONIUM METAL
AS A FUNCTION OF SURFACE AREA PER GRAM

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IGNITION TEMPERATURES OF ZIRCONIUM POWDERS

Point	Sample	Average Particle Size	Ignition temp. °C	°K	Surface Area $\frac{1}{d} \text{ m}^2/\text{gram}$	$\frac{1}{K} \times 10^3$	Log $\frac{1}{d}$
1	Table I-1	2.05	196	469	0.488	2.13	-0.312
2	I-2	2.61	201	474	0.383	2.11	-0.417
3	I-3	2.75	203	476	0.364	2.10	-0.439
4	I-4	3.22	200	473	0.311	2.11	-0.508
5	II-1	6.6	181	454	0.152	2.20	-0.819
6	II-2	6.8	186	459	0.146	2.18	-0.836
7	II-3	5.8	192	465	0.173	2.15	-0.761
8	II-4	5.9	181	454	0.170	2.20	-0.769
9	II-5	6.1	181	454	0.164	2.20	-0.784
10	III-1	33.0	378	651	0.030	1.53	-1.523
11	III-2	18.3	312	585	0.055	1.71	-1.260
12	III-3	3.15	199	475	0.318	2.12	-0.498
13	IV-1	2.5	187	460	0.400	2.18	-0.398
14	IV-II	2.6	158	431	0.385	2.32	-0.415
15	IV-III	4.2	160	433	0.238	2.31	-0.623
16	ZMP 41	0.32	214	487	3.12	2.05	+0.494
17	ZMP 5	0.32	160	433	3.12	2.31	+0.494
18	103-G 3BM	0.32	171	444	3.12	2.25	+0.494
19	ZMP 19	0.85	135	408	1.18	2.45	+0.071
20	ZMP 1105	0.86	222	495	1.16	2.02	+0.064
21	103-G3	1.1	281	554	0.91	1.80	-0.041
22	ZMP 106-1	1.8	222	495	0.555	2.02	-0.256
23	GZ-1	0.87	200	473	1.15	2.12	+0.060
24	GZ-2	3.7	240	513	0.27	1.95	-0.569
25	GZ-3	7.2	500	773	0.139	1.295	-0.857
26	Turnings	$4.4 \times 10^{-3} \text{ m}^2/\text{gram}$	400	673	0.0044	2.50	-2.357
27	Ornutt and Sheer*		190	463	0.200	2.16	-0.699

* Ornutt and Sheer, Trans. Electrochem. Soc. 88 195 (1945).

Their analysis with extensive modifications is as follows;

The experimental equation for the rate of oxidation of zirconium in the range 200-425 C is (10)

$$W^2 = Kt + C \quad (1)$$

where W = weight gain of a sample of known area, in grams of ZrO_2 per unit area.

t = time

K = a reaction rate experimentally determined with Arrhenius temperature dependence; i.e., $K = A e^{-E/RT}$

C = a constant of importance only at the beginning of measurement.

The constant K for a given temperature is determined from a series of experiments in which weight gain is determined as a function of time. The actual magnitude of the rate can vary as a function of how much oxide is present at time $t = 0$.

Differentiation of Equation (1) yields the rate of reaction per unit area,

$$\frac{dW}{dt} = \frac{A^{1/2} e^{-E/2RT}}{2 t^{1/2}} \quad (2)$$

The rate of heat generation, $\frac{dH}{dt}$, will be equal to the product of the rate of reaction per unit area; the area per gram (S), the mass (m) and the heat of reaction per gram of ZrO_2 formed (Q). Thus,

$$\frac{dH}{dt} = \frac{m Q S A^{1/2} e^{-E/2RT_x}}{2 t^{1/2}} \quad (3)$$

where T_x = the temperature of the metal surface of interest, not the ambient temperature.

The surface area per gram, S , of a sphere can be expressed by:

$$S = \frac{6}{d^3 \rho} d^2 = \frac{6}{d \rho} \quad (4)$$

where d is the diameter of the spherical particle and e is the density. Substituting (4) into (3) and combining Q , e , A , m and the integers results in the following expression for the rate of heat generation:

$$\frac{dH}{dt} = \frac{G e^{-E/2RT_x}}{t^{1/2} d} \quad (5)$$

$$\text{where } G \text{ equals } \frac{3 Q A^{1/2} m}{\rho} \quad (6)$$

Thus the rate of heat generation increases with increasing temperature and decreasing particle size and decreases with increasing time.

If the sphere or spheres were insulated such that no heat could escape, the temperature T_x would have to increase at a rate dependent on the heat capacity of the sphere. In all practical ignition experiments however, a loss of heat will occur. Whether the loss of heat is by conduction, convection, or radiation, the loss is essentially proportional to the temperature difference between object and environs, if this difference is small, inversely proportional to the distance between the surfaces:

$$-\frac{dH}{dt} = \frac{J (T_x - T_1)}{r} \quad (7)$$

J = Heat transfer coefficient

T_1 = temperature of ambient or sink

r = distance from T_x to T_1

In the steady state, heat evolved by the reaction must equal heat dissipated to the surroundings, hence

$$\frac{G e^{-E/2RT_x}}{t^{1/2} d} = \frac{J(T_x - T_1)}{r} \quad (8)$$

In exothermic reactions the rates of which are an exponential function of the temperature, there are two possible stable states of reactions:⁽¹⁴⁾

Regime I in which the reaction rate is controlled by thermal kinetics and depends on temperature usually according to an expression such as $Ae^{-E/RT}$; and

Regime II, the upper regime, called the state of active ignition in which the rate of reaction is controlled by diffusion kinetics and almost independent of temperature.

These two situations are illustrated in Figure 2. The temperature T^* at which the system passes abruptly from thermal kinetic control to diffusion kinetic control is the true ignition temperature.

FIGURE 2

Variation of Reaction Mechanism with Temperature

However, in practice the term "ignition temperature" is applied instead to that temperature T_1 , the ambient temperature, in which a sample will ignite. T_1 can be much lower than T^* , but because of the heat buildup, T_x can equal and/or exceed T^* and hence ignition can occur. A solution of equation (8) in terms of T_1 is desirable, but is not simple to achieve, since T_1 is not independent of T_x . If the experiments are performed in such a manner that T_x is approximately equal to T_1 , then we may substitute T_1 for T_x in the exponential term equation (8) and establish a minimum condition for ignition, as

$$\frac{G e^{-E/2RT}}{t^{1/2} d} = \frac{J (\Delta T)}{r} \quad (9)$$

$$\text{or} \quad e^{-E/2RT} = \frac{J d t^{1/2} (\Delta T)}{G r}$$

and taking logarithms

$$\frac{-E}{2 R T_1} = \ln \frac{J d t^{1/2} (\Delta T)}{G r} \quad (10)$$

from which

$$T_1 = \frac{-E}{2 R \ln \frac{J d t^{1/2} (\Delta T)}{G r}} \quad (11)$$

$$\text{or} \quad T_1 = \frac{E}{2 R \ln \frac{G r}{J d t^{1/2} (\Delta T)}} \quad (12)$$

Replacing G by its value (5), and changing to common logs,

$$T_1 = \frac{E}{9.14 \log \frac{3 Q A^{1/2} r m}{J d \rho t^{1/2} (\Delta T)}} \quad (13)$$

From equation (13) the following inferences can be made:

1. The greater the distance, r , that heat must travel to be lost from the sample, the lower the apparent ignition temperature.
2. The greater the mass of sample for any given effective diameter the lower the ignition temperature; i.e. the more powder, the lower the temperature.
3. The smaller the diameter of each particle in the sample, the lower the ignition temperature.
4. The less time it takes to ignite, the lower the apparent ignition temperature; that is the ignition temperature is a function of the heating rate.
5. If at any given ambient temperature T_1 a small sample (M small) does not ignite in a short time, it probably won't ignite; conversely, a very large pile of powder may ignite at a low temperature after a very long time.
6. The greater the activation energy for the oxidative reaction, the higher the ignition temperature.
7. The greater the heat produced per gram of oxide formed, the lower the ignition temperature.
8. The less dense the sample the lower the ignition temperature.
9. The better insulated the sample, the lower the ignition temperature.
10. The larger the A value of the rate expression the lower the ignition temperature.
11. Ignition will occur at that place which reaches T^* first, usually in the interior of a powder sample, not necessarily the center, since oxygen depletion might occur to such an extent that the hottest place is between the center and the exterior face. Massive samples will usually ignite near a corner where radiative heat transfer is poorest.

Finally, the equation (13) may be rearranged as follows:

$$\frac{1989}{T_1} = \log \left(\frac{1}{d} \right) + \log \frac{3 Q A^{1/2} r m}{J \rho t^{1/2} (\Delta T)} \quad (14)$$

where the value of 18.2 Kcal/mol for ZrO_2 has been inserted.

For systems in which Q , A , J , ρ , t , and m are roughly comparable, a plot of $\log \frac{1}{d}$ against $\frac{1}{T_1}$ should be a straight line.

Massive metal sheets of an effective d of about 5000 microns ignite around 1000 C.⁽¹¹⁾

Such a system should have an ignition temperature close to a true estimate of ignition temperature as derived above. A line of slope 1989 passing through the point $\frac{1}{d} = 2 \times 10^{-4}$ and $T = 1000$ C lies just below all experimentally observed points of Anderson and Belz just as the theory would predict. The points all lie above this line because of the inherent difficulty in establishing exactly reproducible conditions for minimum ignition. Almost every conceivable situation such as conditioning and rate of heating will act to increase the apparent ignition temperature.

EFFECTS OF CONDITIONING AND RATE OF HEATING

It has been noticed repeatedly in the zirconium powder industry that continuous exposure to air either in diluted form or at low temperatures can apparently increase the ignition temperature. The easiest way to look at the effect is through the Arrhenius rate expression

$$\text{Rate} = A e^{-E/RT}$$

In general, the condition of the surface of the particle will not change the value of E for the actual basic rate expression of oxygen reacting with zirconium. However, it does change the actual observed rate from a linear

dependence on time to a parabolic dependence; i. e.,

$$W^2 = K t + C \quad \text{and}$$

$$\frac{dW}{dt} = \frac{K^{1/2}}{2t^{1/2}}$$

which says that the rate of reaction and hence, the heat generated, decreases with increasing time.

The net effect of the parabolic oxidation rate is that the effective value of A will become less as the oxide film builds up. Therefore, any conditions which can build up an oxide film on the surface will lower A and hence increase the apparent ignition temperature. In practice, this is accomplished by exposing clean, fresh metal surfaces to a gradually increasing concentration of oxygen or holding the sample for longer periods below the ignition temperature. Some experimental supporting evidence is presented in the following section.

EXPERIMENTS WITH TURNINGS AND FILINGS

Lathe turnings are a constant source of zirconium scrap. It seemed desirable to determine whether such shapes had ignition temperatures as predicted.

Lathe turnings having a surface area of 4 to 5×10^{-3} square meters per gram were wrapped around a small thermocouple and plunged into an oven preset at certain temperatures. The temperature of the thermocouple was recorded and the sample observed. The turnings were clean and bright and a new sample was taken for each test.

Only when samples were plunged into a furnace above 750°C would ignition occur. The ignition was marked by a glow and an inflection in the temperature-time curve. The ignition temperature was $400^\circ\text{C} \pm 25^\circ\text{C}$. However, the furnace was set at 400°C only a brassy, gold tarnish of nitride

formed. At 500 C a blue-black oxide was formed. The same was true for 600 and 700 C; above 750 C, the samples burst into a glow and burned quietly. The region of these tests falls nicely on the line of Figure 1. Also, the effect of conditioning or slow heating rates is easily seen. Unless the temperature rose to 400 C at something like 100/second, enough oxide formed to protect the sample from true ignition. The lowest rate appeared to be about 60/second or roughly 7 seconds exposure and then ignition was erratic. Individual turnings ignited at one end with a torch would frequently ignite, burn a centimeter or so and then go out. The oxidation occurring along the heated strip of turnings was quite evident as a blue-black oxide. Evidently the ignition temperature is so increased by the process that self propagation cannot occur.

Magnesium turnings, on the other hand, ignite readily with a match and self-propagate. Also, molten magnesium at 651 C readily ignites and burns. Here the surface to mass ratio is very low. Magnesium powder of high surface area is not quite as sensitive as zirconium powder; therefore a line on Figure 1 for magnesium would be steeper, crossing the zirconium line somewhere above room temperature.

Iron powder is not nearly as sensitive by a factor of 100 as zirconium, and even molten iron does not ignite. Hence, a line for iron would be more horizontal and cross the room temperature axis at about 100 on the 1/d scale. These numbers are quoted in an attempt to place zirconium in its proper relation to common metals.

A frequent question that is asked is whether it is safe to smoke around zirconium scrap. In general only the finer scrap such as filings and sawdust need be considered.

Filings and sawdust may be classified as 200-325 Tyler screen size or 44-74 microns. Such particles should ignite somewhere between 280 and 310 C., and it is possible that they could be ignited by the glowing red end of a cigarette which is at least 700 C. However, because the heat capacity of metallic zirconium is quite high, and the heat output per unit time of a

smoldering cigarette is very low, usually such ignition did not occur. Occasional small flashes occurred but continued ignition was never observed. However, a definite smoking hazard could exist with sawdust and filings.

EXPERIMENTS PERTINENT TO STORAGE HAZARDS

Piles of clean dry turnings were touched with a torch or had ignited turnings dropped into them. In no instance was continued ignition observed. When turnings covered with a cutting oil like that used on lathes were touched with a torch or had a hot turning dropped into them, the cutting oil would ignite and frequently ignite portions of the metal. Frequently, puffs of smoke and pressure waves would be apparent as volatilized oil exploded.

On the basis of such tests as these, it appears desirable to store turnings and scrap in an oil free condition. The apparent hazard is the oil rather than the metal.

In experiments involving turnings moistened with water, no apparent change in ignition point was visible and the turnings burned as well or better than they did when initially dry. These experiments involved turnings which were just damp. Turnings which were immersed in water have not been tested to determine their ignition point. Higgins⁽¹²⁾ of Aero Jet General has performed experiments pouring molten zirconium and zircalloys into water. As long as the metal remained in large globules, the reaction ceased after a scale formed. If the metal were dispersed, violent explosions occurred. Their method of dispersal could produce about 0.5% of - 200 mesh material. Since lots of filings and sawdust may be of this mesh range, it appears that wet storage may constitute a very great explosion hazard in the event of a fire. It may be that the chance of ignition in wet material may be less than in dry storage. But in the event that wet scrap is involved in an external fire of small level, an extremely violent explosion approaching a low order detonation with shock fronts moving at 1000 to 2000 meters per second is a distinct and real probability. Since dry storage material will just glow and cause only local damage by heat, it appears that clean, dry storage represents

a more practical, realistic and safer approach, than storage under water.

Another factor in water storage which has not been brought to attention is the possibility of isolating pyrophoric powder by the flotation of light particles. Andersen and Belz⁽⁹⁾ have shown that the zirconium which can be decanted with water is very sensitive to ignition. It can be predicted that such particles suspended in water would be deposited in certain preferred locations during the drying out process. Thus, a pile or mass of powder capable of spontaneous combustion under the proper conditions could accumulate. It may be that the Westinghouse fire at Bettis Field had its origin in this mechanism. Several hard rain storms preceded the fire. The rain may have washed the fine powder into one corner of the concrete bay. When the mass dried, the very fine powder could have spontaneously ignited, setting off the remaining stored scrap. Therefore, it appears that storage on concrete pads may have its disadvantages. It appears that storage on a permeable sand bed would be more acceptable, since the water laden with zirconium fines would percolate into the sand where accumulation of powder could not occur.

COMMENTS ON POSSIBLE HAZARDS ASSOCIATED WITH DEGREASING

The act of vapor phase degreasing of zirconium with any of the common degreasing agents is not accompanied by any hazard, as long as massive pieces at least as big in cross section as a normal lathe turning are employed. However, in any industrial shop where large quantities of zirconium are being fabricated and subsequently degreased, it is inevitable that a sludge will accumulate in the bottom of the degreasing tank. Such a sludge will be composed of various greases and tars together with an accumulation of the ordinary metal debris, of very small size, which usually clings to any oily piece of metal. It can be postulated that some fraction of this metallic debris will be of such a particle size that temperatures of 100 - 200 C will cause a reaction to occur. The free energy change between zirconium and any of the degreasing agents is very negative, meaning a spontaneous reaction is theoretically possible if the barrier preventing

reaction is removed. For instance, the free energy change for the reaction,

is -205 Kcal⁽¹³⁾. The comparable reaction with iron,

has a free energy change of -129.8 Kcal, still a very negative value. The ignition sensitivity for iron would be expected to be about 100 times less than for zirconium.

It appears, therefore, that a remote hazard may exist in the degreasing operation by way of the sludge accumulations. If sludge is disposed of daily and a separate bath is used for zirconium degreasing, the probability of explosion is essentially removed. Under the conditions of mixed degreasing, in which all kinds of metal scrap would be mixed with zirconium, it would be virtually impossible to predict the ignition conditions.

COMMENTS ON DISPOSAL

In the event that storage is not desirable and disposal is demanded, it is again preferable that the scrap be dry and clean. Dry, clean scrap may be burned with relative safety; but wet or contaminated scrap may explode without warning during the burning. If possible, it is best to produce the scrap in a dry condition. For example, in fabrication with machine tools air should be used as a coolant.

Burning as a method of disposal may entail serious hazard, and precautions for the protection of personnel should be observed. Although burning of zirconium scrap (other than powder) has seldom if ever led to an explosion, this should not be accepted as universal behavior. Warning should be taken from a recent incident in which thorium metal scrap was being burned to convert it to an oxide for safer storage (a routine procedure). An explosion occurred which resulted in one fatality. A quotation from

Nucleonics (July, 1956) concerning this tragedy stated: "Ordinarily it just glows, but this batch seemed to react rather violently." A further objection to burning is that it is very difficult to burn the metal completely. Partially burnt material, reduction residue, has caused one spontaneous fire at the Albany, Oregon station of the U. S. Bureau of Mines. Burning, if incomplete, may produce scrap of smaller particle size than the original and this may be more hazardous than the scrap from which it was formed. A better method of disposing of fine scrap is to dump it into a permanent body of water where it will eventually oxidize and be dispersed. Zirconium is not toxic to animals or plants, so that such a procedure would cause no contamination. Burial in sand is not too desirable since later movement by machinery may ignite the residues with possible injury to personnel.

CONCLUSIONS AND RECOMMENDATIONS

As a result of all the study on zirconium it may be safely assumed that in all ordinary machine shop operations, zirconium is comparable to magnesium, and safer than uranium. Any massive form of the metal has the very desirable properties for which zirconium is favored. When, however, the surface area per gram approaches 0.1 square meter or 1000 square centimeters, caution must be exercised in how it is handled. Since even filings and most grinding residues do not approach this order of magnitude, most of the residues can be treated as safe. An industrial factor of two on this value means that scrap greater than 500 square centimeters per gram should be handled and stored with caution. Clean, cool, dry storage appears to be the most desirable method of storage, since secondary effects of water and oils appears to be disastrous in some instances. If the Y-12 drums had been dry, two things would have been predicted:

- (1) The material would have been conditioned so as to be less sensitive to ignition;
- (2) The explosion would not have occurred and at the worst only burns would have been suffered.

The major incidents with zirconium have all involved reduction residues, powder, low grade sponge and dirty scrap. It appears that these materials have given the massive, very desirable zirconium a rather bad name.

No evidence of any kind could be found in any of the known incidents of zirconium fires or explosions that new or unknown mechanisms, other than simple oxidative attack by air, water, or oxidizing agents was operating. The known dependence of metal particle size on the reactivity of the metal will successfully predict most, if not all, occurrences. In view of this evidence the following recommendations can be safely made.

1. Machine all zirconium dry with jet of air for cooling.
2. Collect scrap in clean steel pails, preferably covered.
3. Store scrap pails in clean, cool, dry location on sand bed.
4. Dispose of grindings and filings and other small scrap by river disposal, pond disposal, ocean disposal, burning or burying.
5. Treat massive scrap like iron scrap but keep it segregated.
6. Degrease either with soap and water or in small batches with daily clean-out of sludge in regular degreasers.
7. Avoid smoking around small, fine scrap.
8. No stringent health precautions need be taken.
9. Avoid oxidizing agents around zirconium. Heat treat massive metal in salt baths, only after ignition temperature tests have been conducted on the particular salt system.
10. Remember that the hazardous condition for zirconium is very small particle size; this is a condition difficult to attain and generally not present in ordinary fabrication. Powder metallurgy fabricators have separate problems generally well taken care of in their plants.

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