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ALLOYING OF ZIRCONIUM-CONTAINING FUELS WITH ZINC AND MAGNESIUM

R. G. Wymer

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

ALLOYING OF ZIRCONIUM-CONTAINING FUELS WITH ZINC AND MAGNESIUM

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1.0 ABSTRACT

Zirconium-uranium alloys dissolved readily in molten zinc (>800°C), but the resulting alloy did not dissolve completely in nitric acid. The fraction of the uranium remaining in the solids was lower with higher Zn/Zr ratios or when another metal, e.g., magnesium, was added to the melt. In the latter case uranium retention by the nitric acid—insoluble residue was as low as 0.3%, compared to at least 6% when molten zinc alone was the dissolvent.

2.0 INTRODUCTION

An attempt was made to develop an alloying process whereby difficultly soluble power reactor fuel elements might be made into nitric acid—soluble melts. From the nitric acid solution the uranium would be recovered by solvent extraction. Only preliminary studies* were made on zinc alloying of fuel elements containing zirconium. The work was discontinued when other methods being investigated, e.g., dissolution in fused fluoride melts,[1] appeared promising.

Fuel elements clad with zirconium and having a high zirconium content in the core are particularly difficult to dissolve. Typically, such elements are 0.3-in.-thick plates consisting of laminated zirconium or zircaloy-2 cladding on each side of a uranium-zirconium core containing 5 wt % uranium. The laminated construction makes it difficult to recover the unburned uranium without complete dissolution. Dissolution in aqueous fluoride[2] is a practicable scheme that has been

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*This report was originally published as an ORNL internal memorandum, CF-56-4-207. It is being republished as a formal report merely to permit ready dissemination of the information and is not to be construed as a complete study.

carried into advanced development stages. However, the presence of fluoride in the waste from such a process poses serious economic waste disposal problems.

The low melting point of zinc metal (419°C) and the ease with which it forms alloys with zirconium made it a reasonable choice as the alloying metal (Fig. 1). At temperatures above 800°C, where zinc alloys rapidly with zirconium, the vapor pressure of the zinc may be expected to be higher than 0.33 atm (Fig. 2). This need not be a serious problem, since a layer of ZnO on top of the zinc effectively prevents volatilization of the zinc* and is self-healing if broken in the presence of air. Zirconium-zinc alloys have been investigated by Carlson and Borders,[4] and additional work on low-zirconium alloys has been done by Chiotti, Ratliff, and Kilp.[5] Other elements that should alloy as well as or better than zinc, but which were not investigated, are magnesium, cadmium, and lithium. The addition of magnesium to the zinc melt was considered briefly.

3.0 EXPERIMENTAL WORK

The presence of appreciable amounts of a nitric acid—insoluble component in the alloyed material limits the access of the dissolvent to the uranium. The percentage of the alloys that was soluble in nitric acid was therefore considered an indication of the success of the method.

3.1 Procedure

Weighed pieces of zinc and of prototype zircaloy-2-jacketed STR fuel elements (1-3 g, 1-3 cm^2) were placed in a 0.5-in.-dia quartz

*For example, only 1.2% of the zinc was lost from a melt made at 850°C at a Zn/Zr mole ratio of 10/1 in an open crucible over a 22-hr period.

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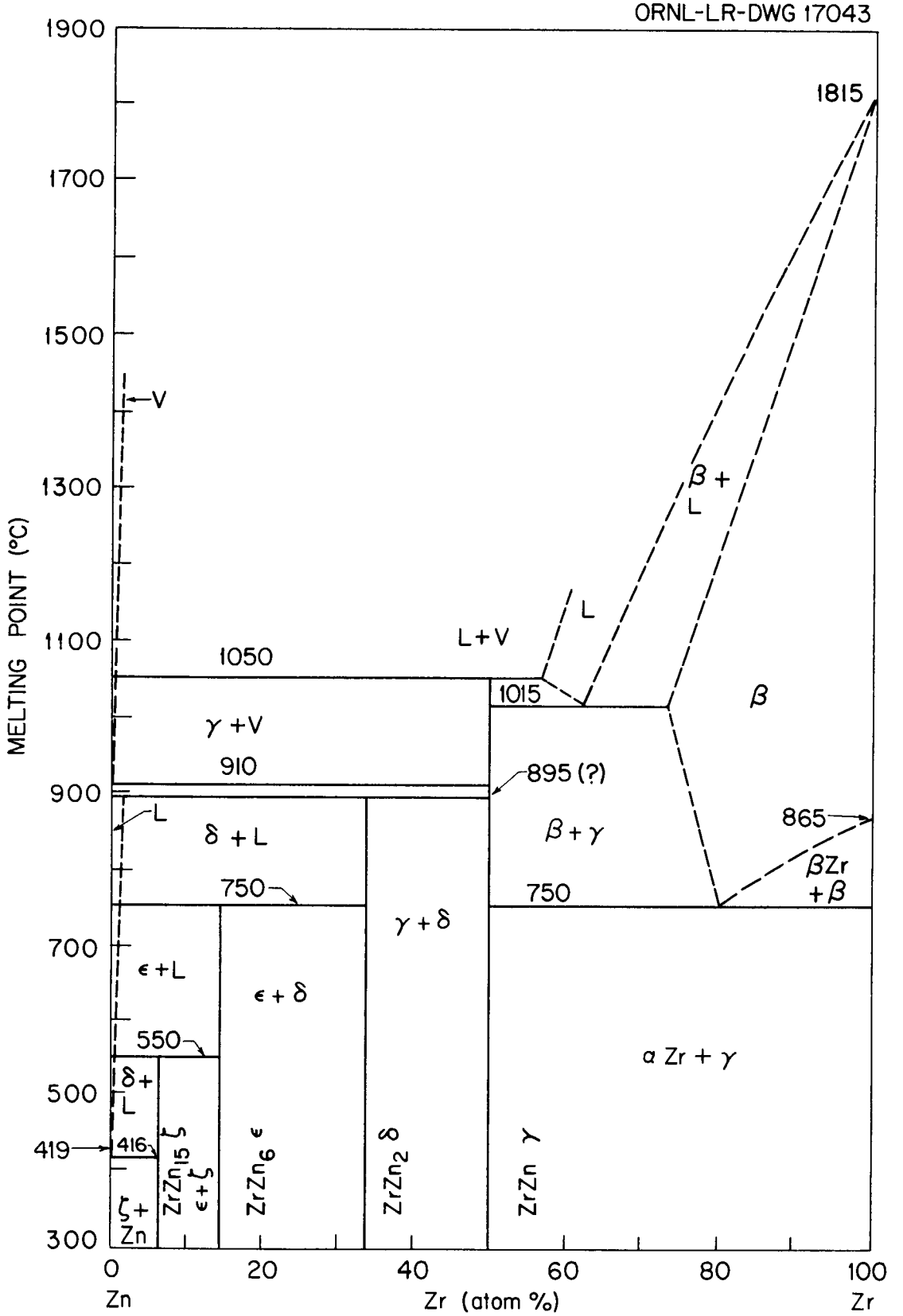

Fig. 1. Tentative Zr-Zn Phase Diagram.

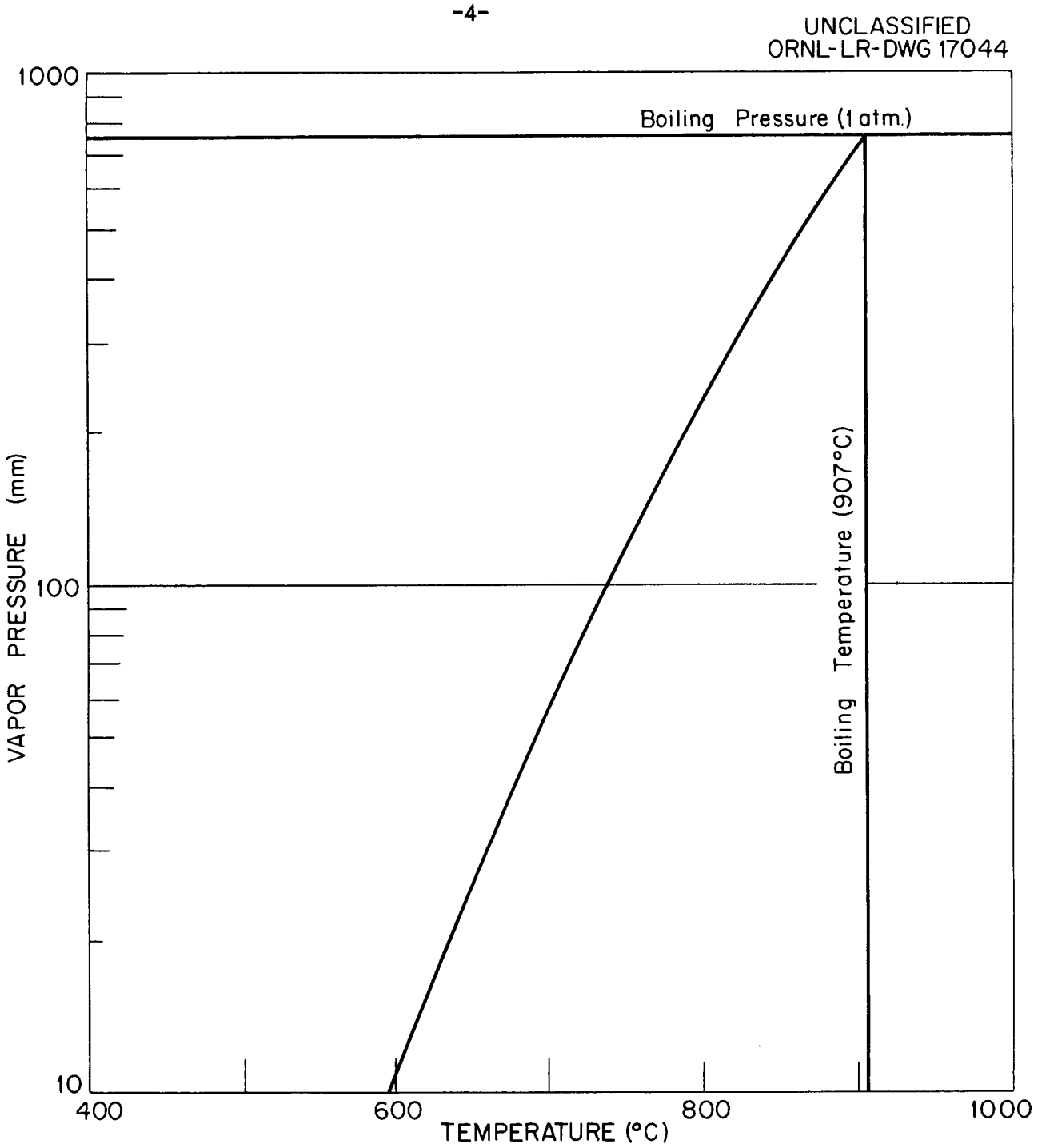

Fig. 2. Vapor Pressure of Zinc Metal.

tube which was evacuated to 15-20 cm Hg absolute and then sealed under vacuum. In several cases the air in the tube was replaced by nitrogen before the evacuation and sealing. The sealed tubes were heated in a furnace. The melts were reacted with boiling 8 M HNO_3 until reaction ceased, after which the solids were filtered off. When ZrO_2 was formed, it was slurried and decanted from the much denser metallic solids before the solids were weighed.

It was necessary for the zinc to penetrate approximately 0.15 cm for complete alloying. Since the uranium-bearing core is innermost, complete alloying is essential for complete uranium recovery.

3.2 Effect of Alloying Time and Temperature and Zn/Zr Ratio*

Times of at least 6 hr and temperatures of at least 850°C appeared to be necessary with Zn/Zr mole ratios of 8/1 for complete alloying. Even under these conditions, 5% of the uranium was not dissolved by the nitric acid treatment (Fig. 3a). More than 16 hr would probably be required for complete alloying at 800°C.

When the melts were made at 800-900°C in a bent tube, using excess zinc, the zinc distilled and separated out in the other end of the tube. The residual melt, which had a Zn/Zr ratio of about 3/1, was practically insoluble in cold nitric acid but dissolved partially in boiling 8 M HNO_3. The insoluble portion of the melt was richer in zirconium than the original melt; if it is assumed that no zirconium dissolved in the nitric acid, the Zn/Zr ratio of the insoluble portion is calculated as 2/1. This assumption is reasonable since no precipitate of hydrolyzed zirconium appeared on boiling.

Very little insoluble uncombined zirconium would be expected in a melt cooled quickly from 800°C. Application of the "lever arm" rule

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*Strictly speaking, the ratios given are those of zinc to fuel element. However, since the elements used are ~95% zirconium, the ratio is considered to be that of zinc to zirconium.

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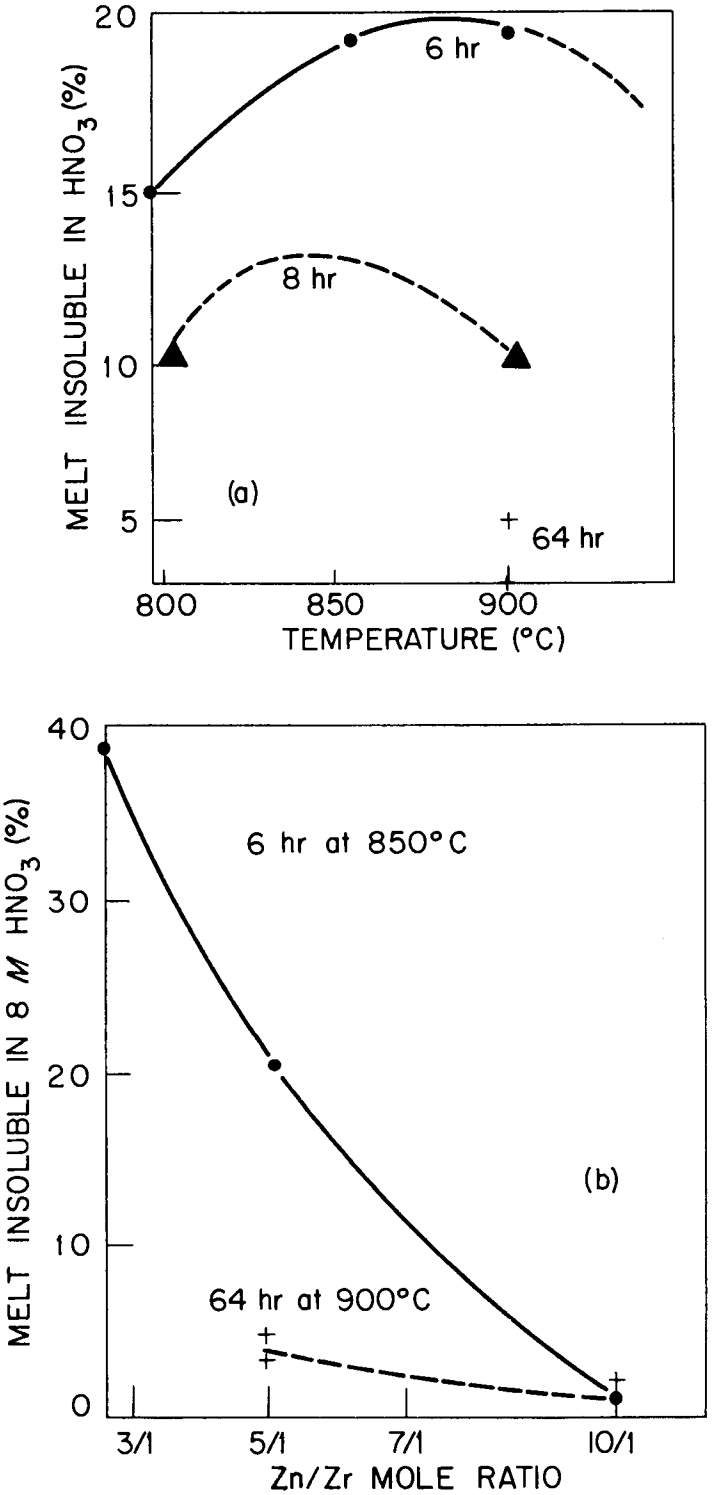

Fig. 3. Melt Solubility as a Function of (a) temperature and time at Zn/Zr mole ratio of 5/1; (b) of mole ratio at given temperature and time.

shows that 3/4 of the moles of zirconium and zinc in the original melt should appear as $ZrZn_2$, and the remaining 1/4 in a zinc-rich phase with a Zn/Zr ratio of 99/1. The latter phase may be assumed to be completely soluble in nitric acid. Actually, the weight ratio of insoluble residue to original sample was 1.43/1.88 = 3/4.

At 850°C the formation of $ZrZn_2$ is more extensive, but more acid-soluble alloy is also formed (Fig. 3b). At 900°C the more easily dissolved alloy is rapidly becoming predominant, as indicated by the dashed line in Fig. 3a. Although based on only two points, this curve shows the nature of the change to be expected with longer alloying times. Since the alloying must occur by a diffusional process, through a thin surface layer, a longer alloying time produces more of the soluble phase if $ZrZn_2$ is the only solid zinc intermetallic present at the temperatures used.

Nitric Acid Requirements for Dissolution of Melts. The data (Table 1) showed that cold 12 M HNO_3 reacts with the alloy melts as follows:

$$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

$$3Zr + 10HNO_3 \longrightarrow 3ZrO(NO_3)_2 + 4NO + 5H_2O$$

Table 1. Nitric Acid Requirements for Dissolution of Melts

Melts prepared by heating zinc + STR prototype fuel element specimens for 25 hr at 900°C

Vol.[a] of 12 M HNO_3 (ml)	Volume (ml)	Final Solution Conc. (M)				Zn/Zr Ratio	
		HNO_3	Zn	Zr	U	Melt	Residue
67.5	64	8.18	1.06	0.123	0.0016	5/1	8.6/1
130.5	121	6.18	2.50	0.145	0.0014	10/1	17/1(?)
94.5	89	6.00	2.36	0.168	0.0015	10/1	14/1
82.3	78	8.30	1.25	0.087	0.0006	10/1	14/1

[a]Volume measured at 25°C.

Dissolution in hot 8 M HNO_3 appeared to be definitely advantageous unless it is desired not to try to dissolve that part of the alloy which is insoluble in cold acid. Dissolution in cold acid has the advantage that very little ZrO_2 is formed during the dissolution, and, if reworking of the uranium-bearing metallic residue is desirable, it could be accomplished with a minimum of difficulty caused by ZrO_2 solids.

3.3 Effect of a Fourth Metal

The addition of a fourth metal, magnesium (runs 22-25), resulted in melts which dissolve in acid with small residues. The uranium loss to these residues is lower by a factor of 10 to 20 than those obtained with zinc alloying alone. Apparently the magnesium displaces the uranium from the postulated uranium-zinc-zirconium alloy product. Uranium losses could probably be reduced still further by varying the fourth metal and/or its amount. A complete resumé of the conditions and results of alloying experiments is shown in Table 2.

Table 2. Zinc Alloying of STR (Zircaloy-2-jacketed) Prototype Element

Alloyings made in sealed quartz tubes evacuated to ~15 cm Hg absolute

No.	Zn/Zr/Mg Mole Ratio	Temp. (°C)	Alloying Time (hr)	Acid Treatment	Melt Insoluble in HNO_3 (%)	U Loss in Solids (%)
1	2/1/0	800	8	Boiling 8 M HNO_3	82	---
2		900	8	Boiling 8 M HNO_3	93	56
3	3/1/0	800	8	Boiling 8 M HNO_3	21	---
4		850	6	Boiling 8 M HNO_3	39	---
5		900	8	Boiling 8 M HNO_3	22	6 (?)
6	5/1/0	800	6	Boiling 8 M HNO_3	15	---
7		800	8	Boiling 8 M HNO_3	11	---
8		800	16	Boiling 8 M HNO_3	25	---
9		800	70.5	Boiling 8 M HNO_3	Small residue	---
10		850	4	Boiling 8 M HNO_3	16	---
11		850	6	Boiling 8 M HNO_3	20	---
12		850	8	Boiling 8 M HNO_3	26	---
13		900	6	Boiling 8 M HNO_3	19	---
14		900	8	Boiling 8 M HNO_3	10	7
15		900	25	8 M HNO_3, 20°C	68	43
16		900	25	12 M HNO_3, unheated	40	16
17		900	64	Boiling 8 M HNO_3	3.6	---
18		900	64	Boiling 8 M HNO_3	5.4	---
19	8/1/0	850	6.5	Boiling 8 M HNO_3	5.6	1 (?)
20		850,700[a]	16,2[a]	Boiling 8 M HNO_3	2.3	11
21		850,700[a]	16,2[a]	Boiling 8 M HNO_3	2.4	11
22	8/1/2.16	850	20	Boiling 8 M HNO_3	4.9	1.9
23		850	20	Boiling 8 M HNO_3	5.4	36 (?)
24[b]		850	16	Boiling 8 M HNO_3	5.2	0.72
25[b]		850	16	Boiling 8 M HNO_3	0.14	0.27
26	8/1/0	850	22.5	Boiling 8 M HNO_3	0.9	6.6

Table 2. (Cont.)

No.	Zn/Zr/Mg Mole Ratio	Temp. (°C)	Alloying Time (hr)	Acid Treatment	Melt Insoluble in HNO_3 (%)	U Loss in Solids (%)
27	10/1/0	800	16	Boiling 8 M HNO_3	3.4	---
28		800	16	Boiling 8 M HNO_3	1.34	---
29		800	70.5	Boiling 8 M HNO_3	Very small residue	---
30		850	6	Boiling 8 M HNO_3	1.5	---
32		900	25	12 M HNO_3, 20°C	8.8	10
33		900	25	12 M HNO_3, unheated	10	8.8
34		900	25	12 M HNO_3, unheated	6.6	10.3
35		900	25	12 M HNO_3, unheated	3.0	16 (?)
36		900	64	Boiling 8 M HNO_3	1.9	---
37	15/1/0	800	16	Boiling 8 M HNO_3	0.6	---
38		800	16	Boiling 8 M HNO_3	0.5	---
39	20/1/0	815	3	Boiling 8 M HNO_3	Alloying had begun	---
40[c]	5/1/0	800	16	Boiling 4 M HNO_3	58	---
41[c]		800	16	Boiling 8 M HNO_3	5	---
42[c]		800	16	Boiling 12 M HNO_3	12	---

[a]Heated at 850°C for 16 hr; then cooled to 700°C and held 2 hr.

[b]Melts prepared by evacuating the quartz tubes to 15-20 cm Hg of air and then refilling with oil-pumped nitrogen to slightly more than atmospheric pressure; repeated three times so that final pressure was 15-20 cm Hg of nearly pure nitrogen.

[c]Acid dissolutions made on different portions of the same melt.

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3. Figure 3 was obtained in a private communication from a group under Dr. Spedding at Iowa State College and represents a modification, resulting from more recent work, of an earlier tentative phase diagram; see B. Lustman and F. Kerze, "Metallurgy of Zirconium," p. 482, Vol. 4, Div. VII, National Nuclear Energy Series, McGraw-Hill, New York.

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