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**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

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**MINES BRANCH INVESTIGATION REPORT IR 65-76**

**DISPERSION-STRENGTHENING  
OF ZIRCONIUM**

**PROGRESS REPORT NO. 1**

by

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**PHYSICAL METALLURGY DIVISION**

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C. F. Dixon\* and H. M. Skelly\*\*

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SUMMARY

This report describes preliminary work done on attempts to dispersion-strengthen zirconium by direct addition of refractory compounds to the arc-melted metal. The following compounds were added in powder form to the zirconium:  $\text{ThO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CeZrO}_4$  and  $\text{MgZrO}_3$ . The tensile strength of the zirconium at  $650^\circ\text{C}$  ( $1200^\circ\text{F}$ ) was significantly improved by each addition, the greatest improvement being obtained with  $\text{ThO}_2$ .

Although it is not certain that true dispersion-strengthening of the zirconium was achieved, the results are considered sufficiently encouraging to justify further work.

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## 1. INTRODUCTION

Since the advent of atomic energy, considerable effort has been expended on the development of improved zirconium alloys for use in nuclear reactors, and the search continues for suitable high-temperature alloys that will enable future reactors to operate at even higher temperatures than at present, with consequent increased efficiency.

The Nuclear and Powder Metallurgy Section has been engaged in zirconium alloy development for several years, and recently consideration has been given to the possibility of improving the mechanical properties of zirconium by dispersion-strengthening it. The first part of this work was concerned with attempts to strengthen zirconium alloys by internal oxidation, but the results were inconclusive and are not considered here.

The internal oxidation work led to investigation of the possibility of dispersion-strengthening zirconium by direct addition of refractory compounds to the molten metal, and this Progress Report describes the work done to date using this technique.

The following refractory compounds were chosen for addition to the zirconium, mainly because of their high stability:  $\text{ThO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CeZrO}_4$  and  $\text{MgZrO}_3$ . Although the presence of thorium is not desirable in a nuclear reactor alloy and it - and lanthanum - have comparatively high neutron capture cross-sections, it was decided to include the oxides of these elements because of their exceptional stability and the good possibility they provided of testing the validity of the idea.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Preparation of Test Specimens

The materials used in preparing the test specimens are listed in Table 1. The reactor grade sponge zirconium contained 0.09% oxygen. The refractory compounds were in powder form.

TABLE 1

Materials Used In Preparing Test Specimens

Material	Purity	Source
Sponge zirconium	Reactor grade	Carborundum Metals Co.
Zircaloy-2	Reactor grade	Atomic Energy of Canada Ltd.
Thorium oxide ( $\text{ThO}_2$ )	'Purified'	Anachemia Chemicals Ltd.
Yttrium oxide ( $\text{Y}_2\text{O}_3$ )	99%	Bernard Ring Inc.
Cerium zirconate ( $\text{CeZrO}_4$ )	99%	Allis-Chalmers Mfg. Co.
Magnesium zirconate ( $\text{MgZrO}_3$ )	91%	Allis-Chalmers Mfg. Co.
Lanthanum oxide ( $\text{La}_2\text{O}_3$ )	99.9%	Davison Chemical Co.
Cerium oxide ( $\text{CeO}_2$ )	Reagent grade	Anachemia Chemicals Ltd.

Except for the Zircaloy-2, which was taken from a piece of commercially-produced tubing, all the "alloys"\* were prepared in a tungsten-arc furnace. Melting and "alloying"\* were carried out by striking an arc between the tungsten electrode and the charge contained in a water-cooled copper hearth. An atmosphere of argon at a pressure of 350 mm mercury was maintained during melting. Each charge was remelted at least three times to ensure homogeneity, and the final ingot was "cigar-shaped" and weighed about 75 g. Prior to addition of the refractory compounds, the zirconium sponge was melted several times to purify and consolidate it.

The refractory powders were dried at 100°C (212°F), briquetted, and stored in a desiccator until ready for alloying, when the briquetted powder was either inserted into a cavity drilled in the zirconium or placed on the copper hearth and covered by the zirconium, which was then melted

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\* Although the terms "alloys" and "alloying" are used in referring to the zirconium-refractory compositions, it is realized that, strictly speaking, these materials may not be true alloys in the classical meaning of the word.

over the briquette.

Table 2 lists the nominal compositions of all the melts prepared in the arc furnace. The volume percentage figures given in the Table were calculated from the true density values for the refractory compounds, except in the case of yttrium oxide and cerium and magnesium zirconates, the true densities of which were not known.

TABLE 2  
Composition of Arc Furnace Melts

Melt Ident.	Addition	Nominal Composition	
		Weight, %	Volume, %
KE	ThO <sub>2</sub>	0.7	0.5
KF	ThO <sub>2</sub>	0.7	0.5
KG	ThO <sub>2</sub>	0.7	0.5
LD	Y <sub>2</sub> O <sub>3</sub>	0.74	-
MI	CeZrO <sub>4</sub>	1.0	-
LO	MgZrO <sub>3</sub>	0.54	-
LG	La <sub>2</sub> O <sub>3</sub>	1.1	1.1
KO	CeO <sub>2</sub>	0.57	0.5

## 2.2 Fabrication and Heat Treatment

All the arc-melted samples were successfully hot swaged at 500°C (930°F) to 0.35 in. diameter rod except sample LG (Zr-1.1% La<sub>2</sub>O<sub>3</sub>), which broke. The pieces from sample LG were remelted to ingot and tested in the as-cast condition.

Specimens of the Zr-0.7% ThO<sub>2</sub> alloy (melt KE) were heat treated in air at 600°C (1110°F) for 6 hr, and additional specimens of this composition

(from melts KG and KF) were sealed in vacuo in quartz capsules and heat treated at 700°C (1290°F) and 800°C (1470°F), respectively.

### 2.3 Microexamination

Samples containing thorium oxide were prepared for microexamination by rough polishing on silicon carbide paper to 600 grit followed by chemical polishing by swabbing with a solution containing 45 parts by volume water, 45 parts by volume nitric acid and 8 to 10 parts by volume hydrofluoric acid.

### 2.4 Mechanical Testing

Mechanical tests were carried out on specimens in the hot-swaged condition for all the alloys except Zr-1.1% La<sub>2</sub>O<sub>3</sub>, which was tested in the as-cast condition. Specimens containing 0.7% ThO<sub>2</sub> were also tested after heat treating at 700°C (1290°F) and 800°C (1470°F). All mechanical tests were carried out at 650°C (1200°F) in a vacuum of 5 x 10<sup>-5</sup> mm mercury, using an Instron universal testing machine. The test specimens were machined to PMD Drawing No. 106, and had a total length of 1.925 in., a gauge length of 1 in., and a gauge diameter of 0.160 in.

## 3. EXPERIMENTAL RESULTS

### 3.1 Microexamination

The as-cast microstructure of the Zr-0.7% ThO<sub>2</sub> composition consisted of particles of a dispersed phase present mainly at grain boundaries and crystallographic planes. This structure was unchanged after heat treating at 600°C (1110°F) for 6 hr and is illustrated in Figure 1.

Figure 2 illustrates the microstructure of the Zr-0.7% ThO<sub>2</sub> composition after swaging and then heat treating at 700°C (1290°F) for 6 hr; the dispersed phase is aligned parallel to the swaging direction.

Figure 3 is an electron micrograph of a Zr-0.7% ThO<sub>2</sub> tensile specimen that had been heat treated at 700°C (1290°F) for 6 hr and then tested at 650°C (1200°F); the discrete particles of the dispersed phase can be clearly seen.

On heating the Zr-0.7% ThO<sub>2</sub> composition to 800°C (1470°F), the dispersed phase concentrated more at the grain boundaries as can be seen by comparing Figure 4 with Figure 2. The grain boundary concentrations are shown at higher magnification in Figure 5.

### 3.2 Tensile Tests

Table 3 lists the tensile properties of the zirconium-refractory compositions at 650°C (1200°F). Also included in Table 3 are the mechanical properties of Zircaloy-2 as determined in these laboratories and of zirconium as given in reference No. 1.

TABLE 3

Tensile Properties of Zirconium and Alloys at 650°C (1200°F)\*

Melt Ident.	Nominal Composition	Condition	UTS (kpsi)	0.2% YS (kpsi)	%El on 1 in.
KE	Zr-0.7% ThO <sub>2</sub>	As-Swaged	24.5	14.8	46
KF	Zr-0.7% ThO <sub>2</sub>	H. T. 800°C (1470°F) 6 hr	16.2	9.4	62
KG	Zr-0.7% ThO <sub>2</sub>	H. T. 700°C (1290°F) 6 hr	23.6	14.7	48
LD	Zr-0.74% Y <sub>2</sub> O <sub>3</sub>	As-Swaged	12.6	7.3	76
MI	Zr-1.0% CeZrO <sub>4</sub>	As-Swaged	19.9	11.9	36
LO	Zr-0.54% MgZrO <sub>3</sub>	As-Swaged	14.9	8.3	67
LG	Zr-1.1% La <sub>2</sub> O <sub>3</sub>	As-Cast	19.8	12.5	31.5
KO	Zr-0.57% CeO <sub>2</sub>	As-Swaged	11.1	7.2	43
-	Zircaloy-2	As-Received	17.0	11.9	21
-	Zirconium	As-Extruded	8.6	8.4	37.5

\* Results listed are averages of three tests, except for LG (average of two tests) and "Zirconium" (from reference No. 1).



#### 4. DISCUSSION

The microstructure of the Zr-0.7% ThO<sub>2</sub> composition in the as-cast condition (see Figure 1) indicates that a constituent that had been in solution in the zirconium precipitated out as discrete particles on crystallographic planes of the beta phase during cooling; this microstructure was unchanged after heating at 600°C (1110°F) for 6 hr (see also Figure 1). Hot swaging followed by heat treating at 700°C (1290°F) for 6 hr resulted in some recrystallization but, as Figure 2 illustrates, the dispersed phase persisted unchanged except that it was re-orientated in the direction of swaging. Figure 4 shows that heating the swaged material at 800°C (1470°F) for 6 hr resulted in coalescence of the dispersed phase and further recrystallization of the zirconium. The coalesced phase present in Figure 4 is still orientated to some extent with the swaging direction.

The tensile properties of the Zr-0.7% ThO<sub>2</sub> composition (Table 3) are consistent with the microstructures. There was little change in the strength of the as-swaged material after heating at 700°C (1290°F) for 6 hr, but heating at 800°C for 6 hr caused a large drop in properties. As Table 3 shows, all the refractory additions effected some improvement in the elevated temperature tensile strength of the zirconium, the greatest improvement resulting from ThO<sub>2</sub>, followed by CeZrO<sub>4</sub> and La<sub>2</sub>O<sub>3</sub>, and then Y<sub>2</sub>O<sub>3</sub>, MgZrO<sub>3</sub> and CeO<sub>2</sub>.

As indicated in Table 3, the compositions tensile tested were in various conditions, but it is considered that the heating involved in testing the specimens at 650°C (1200°F) would stress-relieve them <sup>(4)</sup>.

It is possible that at least part of the refractory compound addition was decomposed during preparation of the compositions in the arc furnace and, in this event, some oxygen would dissolve in the zirconium and strengthen it at room temperature. However, it is considered that any strengthening effect resulting from oxygen picked up by the zirconium would be negligible at the testing temperature, namely, 650°C (1200°F) <sup>(1, 5)</sup>. It is more likely that, if decomposition of the refractory compounds occurred, there would be some solution strengthening from the metallic constituent of the compounds. Another possibility is that the refractory compounds were partially decomposed, resulting in the formation of a sub-oxide.

It is not certain that dispersion-strengthening of zirconium has been achieved in this preliminary investigation, and it is planned to carry out more work to determine what reactions occur during arc-melting and to study the properties of the present, and other compositions, more fully.

It is obvious from the electron-micrograph shown in Figure 3 that considerable improvement can be made in the size, distribution, and amount of the dispersed phase.

Work has been done elsewhere<sup>(2)</sup> on the dispersion-strengthening of metals by mixing them, in powder form, with very fine powders of refractory compounds and compacting and extruding the mixture. Zirconium<sup>(1)</sup> and titanium<sup>(3)</sup> are among the metals that have been investigated in this manner. However, the technique described in this report has the advantage that it does not involve the handling of zirconium powder, which requires special precautions because of its reactivity.

## 5. CONCLUSIONS

1. The tensile strength of zirconium at 650°C (1200°F) was improved by the direct addition of  $\text{ThO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CeZrO}_4$  or  $\text{MgZrO}_3$  to the metal when melted in a cold-hearth, inert gas, arc-melting furnace.
2. Of the refractory compounds added,  $\text{ThO}_2$  resulted in the greatest improvement in the elevated temperature tensile strength of the zirconium.

## 6. FUTURE WORK

Future work will include tests on other zirconium-refractory compositions. The nature of the dispersed phase will be investigated, and attempts made to improve its size and distribution.

## REFERENCES

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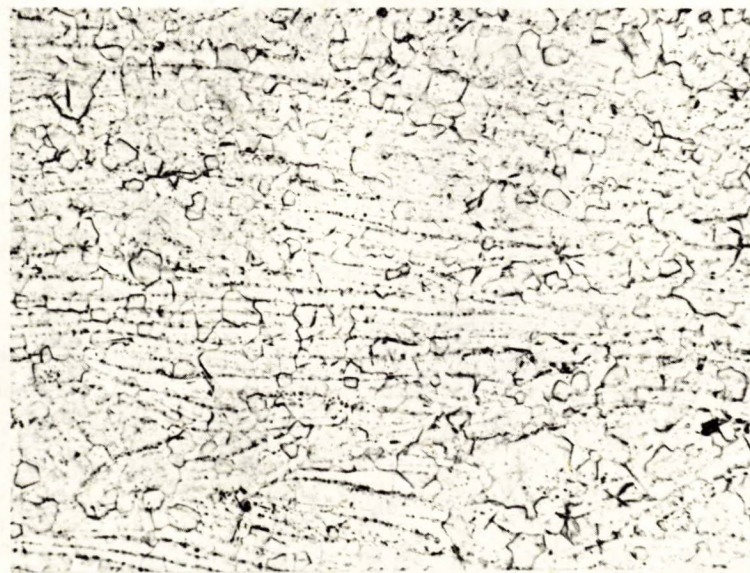
3. "Dispersion Hardening of Sintered Titanium Alloys by Refractory Metal Powder Additions" - Final Report, Project B093, Armour Research Foundation (Mar. 5, 1958).
4. G. L. Miller, "Zirconium" - Butterworth's Scientific Publications, London, 2nd ed. 471 (1957).
5. Ibid. pp. 252-253.

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150X

Figure 1. Zr-0.7% ThO<sub>2</sub> (Melt KE).  
Heat treated 600°C (1110°F) 6 hr.  
(No change from as-cast microstructure).



150X

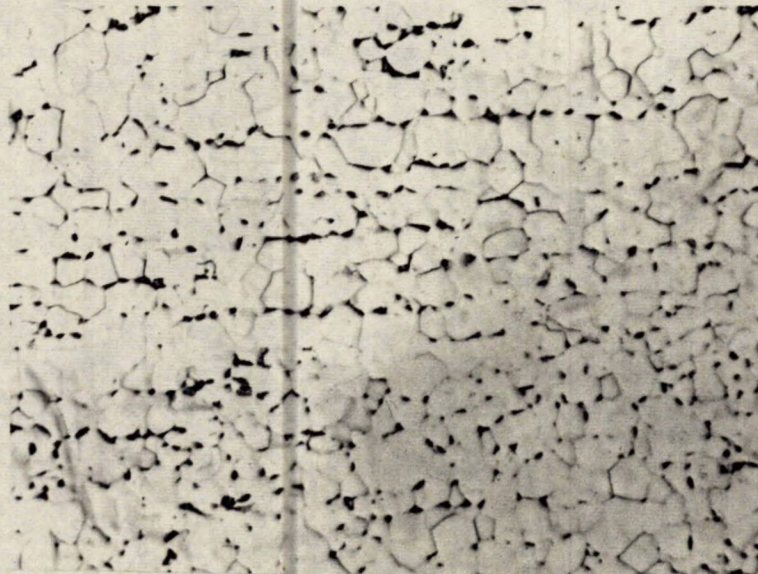
Figure 2. Zr-0.7% ThO<sub>2</sub> (Melt KG).  
Swaged and heat treated 700°C.  
(1290°F) 6 hr.





6,000X

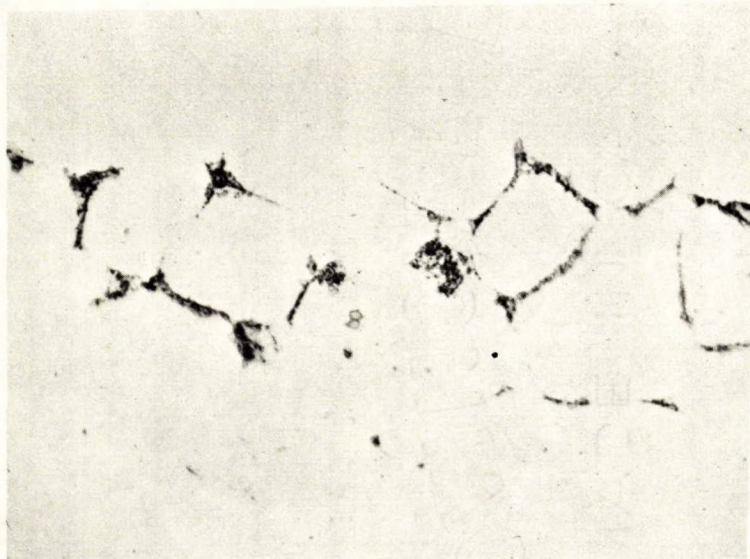
Figure 3. Zr-0.7% ThO<sub>2</sub> (Melt KG).  
Heat treated 700°C (1290°F) 6 hr.  
(Tensile tested at 650°C (1200°F)).  
Electron micrograph.



150X

Figure 4. Zr-0.7% ThO<sub>2</sub> (Melt KF).  
Swaged and heat treated 800°C.  
(1470°F) 6 hr.





750X

Figure 5. Zr-0.7% ThO<sub>2</sub> (Melt KF).  
Heat treated 800°C (1470°F) 6 hr.