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DEVELOPMENT OF ZIRCONIUM ALLOYS.
PART I

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August 8, 1951

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2

BATTELLE MEMORIAL INSTITUTE

Columbus, Ohio

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PART I

Contract No. W-7405-eng-92

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	4
INTRODUCTION	5
EXPERIMENTAL WORK	6
Fabrication of the Alloys	6
Tensile Testing	8
Microstructure	16
Corrosion Data	16
Transformation Temperatures	16
Heat-Treating Data	17
CONCLUSIONS	20
APPENDIX.	21
Calculation of the Neutron Cross Section of an Alloy	21

DEVELOPMENT OF ZIRCONIUM ALLOYS

SUMMARY

A number of alloys of zirconium have been investigated as part of a program aimed at improving the high-temperature tensile strength of zirconium. These alloys include molybdenum, tantalum, tungsten, tin, titanium, and nitrogen alloys. It was found that small additions of molybdenum, tantalum, tin, titanium, and nitrogen appreciably increase the high-temperature tensile strength of zirconium.

INTRODUCTION

The development of high-temperature alloys of zirconium at Battelle Memorial Institute is being carried out at the request of the Knolls Atomic Power Laboratory. It is desired to produce a zirconium alloy of high creep resistance and low neutron-absorption properties. The alloy is to be used as structural material in place of stainless steel, Type 347, and, therefore, any such alloy must be as strong as stainless steel and have a lower neutron cross section. In addition, the alloy should have sufficient hot workability to enable it to be fabricated into simple shapes.

For the purposes of this investigation it was decided to attempt to increase the strength of zirconium at 500 C. Since this temperature is near the lowest recrystallization temperature of pure zirconium, any improvement in the strength of zirconium at this temperature should result in improved strength both above and below this temperature.

Since, in a program of this sort, there are a large number of alloys to evaluate, it is desirable to screen the alloys using some short-time test. For this reason the tensile properties, including 0.2 per cent yield strength, have been determined at 500 C and the alloys are evaluated on the basis of their relative yield strengths. An acceptable alloy must have a yield strength at 500 C equal to that of stainless steel, Type 347, and a neutron cross section less than one-third that of a stainless steel.

EXPERIMENTAL WORK

A. Fabrication of the Alloys

The zirconium used in this program was Foote Mineral Company iodide zirconium. This zirconium was not the highly corrosion resistant grade, since corrosion resistance was of minor interest in this program. The alloying elements used were of high purity.

The alloys were prepared in non-outgassed graphite crucibles in an absolute pressure of less than ten microns of mercury. The materials were charged into the crucibles and melted. In most cases, the minor alloys were placed in holes drilled in the zirconium pieces and sealed in with zirconium chips.

The as-cast alloys were hot rolled at 850 C to slabs 1/8 inch thick. These slabs were scalped to approximately 0.10 inch and cold rolled to approximately 0.080 inch. The cold-rolled alloys were annealed in a straightening press for seven hours at 650 C. The resulting zirconium-alloy sheet was machined to 0.060 inch and cut into tensile specimens. Hardness data and chemical analyses for the first set of alloys prepared under this program are shown in Table I.

Observations made during the hot rolling indicated various trends in the behavior of these alloys to hot deformation. It was observed that the alloys containing nitrogen tended to be hard and brittle. There was one exception, the nitrogen-bearing tungsten alloy. The titanium alloys exhibited good ductility and the addition of aluminum to these alloys caused heat to generate during exposure to air in the rolling process.

TABLE I. HARDNESS DATA AND CHEMICAL ANALYSES
FOR THE FIRST SET OF ALLOYS

Zirconium Alloys, Weight Per Cent (As Analyzed)	Rockwell "A" Hardness		
	As Cast	Cold Rolled	Annealed 7 Hours at 650 C
0.26 C	43	49	44
0.27 C	58	51	43
0.82 Mn + 0.25 C	51	59	49
1.05 Sn + 0.24 C	49	54	49
1.35 Sn + 0.22 C	48	56	51
3.0 Ta + 0.44 C	47	52	50
6.4 Ta + 0.56 C	48	55	53
0.45 W + 0.30 C	46	49	45
0.30 W + 0.23 N + 0.14 C	62	63	61
1.6 Ti + 0.21 C	50	54	47
3.4 Ti + 0.18 N + 0.25 C	63	61	60
10.4 Ti + 0.34 C	62	60	57
49 Ti + 0.5 Al + 1.1 C	68	66	63

The tantalum and tungsten alloys probably require higher working temperatures, for some tearing was noticed. The molybdenum alloy appeared to work well and had very little surface contamination when compared with the rest of the alloys.

In a very general way, the annealed hardnesses of these alloys agree with their tensile strengths. Alloys with an annealed Rockwell "A" hardness of less than 50 are quite weak; alloys with an annealed Rockwell "A" hardness of greater than 60 show considerable strength; alloys with annealed Rockwell "A" hardness of 50 to 60 may or may not be strong.

B. Tensile Testing

The tensile specimens prepared for this work had a 1-1/2-inch reduced section, were 0.50 inch wide in the reduced section, and were approximately 0.060 inch thick. Specimens were taken parallel to the rolling direction. These specimens were tested at 500 C in an argon atmosphere. The speed of travel of the head of the testing machine was 0.02 inch per minute. An extensometer with a 1-inch gage length and an accuracy of plus or minus 0.0001 inch per inch was used to measure extensions. This extensometer was of the clip-on type utilizing SR-4 gages with slide bars extending out of the heated area around the specimen.

The data from these tensile tests are shown in Table II. The true stress, true strain curves for significant alloys are shown in Figures 1, 2, and 3. The strain-hardening exponent, "n", is the slope of the plastic stress-strain curves shown in Figure 4. The constant "B" is the true

TABLE II. DATA FROM TENSILE TESTS

Zirconium Alloys, Weight Per Cent (As Analyzed)	Tensile Properties at 500 C					
	Per Cent Offset, 1000 psi	Ultimate Strength, 1000 psi	Per Cent Elongation In 1 Inch	Per Cent Reduction of Area	Strain- Hardening Exponent "n"	B, 1000 psi
0.26 C	11.2	21.5	45	55	0.15	35
0.27 C	9.8	17.2	45	53	0.17	28
0.82 Mo + 0.25 C	14.5	24.3	52	62	0.15	38
1.05 Sn + 0.24 C	14.2	22.5	50	53	0.17	36
1.35 Sn + 0.22 C	15.9	22.9	49	60	0.14	34
3.0 Ta + 0.44 C	21.5	28.0	21	32	0.07	35
6.4 Ta + 0.56 C	27.0	32.8	24	46	0.06	41
0.45 W + 0.30 C	10.4	16.0	26	56	0.14	22
0.30 W + 0.23 N + 0.14 C	16.2	26.9	50	52	0.16	40
1.6 Ti + 0.21 C	14.2	28.6	31	49	0.23	44
3.4 Ti + 0.18 N + 0.25	29.9	46.8	30	39	0.13	73
10.4 Ti + 0.34 C	41.2	58.3	33	45	0.13	84
49 Ti + 0.5 Al + 1.1 C	60.0	86.7	1	3	0.19	-

FIGURE 1. TENSILE PROPERTIES OF ZIRCONIUM ALLOYS AT 500 C

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FIGURE 2. TENSILE PROPERTIES OF ZIRCONIUM ALLOYS AT 500 C

FIGURE 3. TENSILE PROPERTIES OF ZIRCONIUM ALLOYS AT 500 C

FIGURE 4. PLASTIC STRAIN HARDENING CURVES FOR ZIRCONIUM ALLOYS AT 500 C

stress when the true strain is equal to unity. These are the coefficients of the empirical relation, $\sigma = B \delta^n$, where σ is the true stress and δ is the true strain.

The best alloys in this group appear to be the 6.4 per cent tantalum alloy, the 3.4 per cent titanium plus 0.18 per cent nitrogen alloy, and the 10.4 per cent titanium alloy.

In order to compare alloys with respect to their yield strengths and thermal neutron capture cross sections, the thermal neutron capture cross section of each alloy was calculated by the method shown in the Appendix. Then the ratio of the yield strength of each alloy to the yield strength of stainless steel was calculated. The yield strength of Type 347 stainless steel at 500 C is approximately 31,000 psi*. Then the ratio of the neutron capture cross section of each alloy to the cross section of stainless steel was calculated. The neutron capture cross section of Type 347 stainless steel is taken to be approximately 2.86 barns per atom. The ratios of the yield strengths and cross sections are shown in Table III.

These results indicate also that the 6.4 per cent tantalum alloy, the 3.4 per cent titanium plus 0.18 per cent nitrogen alloy, and the 10.4 per cent titanium alloy are the best alloys. The 49 per cent titanium plus 0.5 per cent aluminum alloy may be disregarded because its ductility is very low and its cross section high. It is interesting to note, however, that this alloy is nearly twice as strong as stainless steel and it was workable. The reason for its low ductility may lie in some precipitation process resulting from the cold work and annealing.

*C. T. Evans, "Wrought Heat Resisting Alloys for Gas Turbine Service", Metals Progress, November, 1945, p. 1085.

TABLE III. PROPERTIES OF ZIRCONIUM ALLOYS
COMPARED WITH STAINLESS STEEL

Zirconium Alloys, Weight Per Cent (As Analyzed)	Thermal Neutron Capture Cross Section, Barns/Atom	Yield Strength Ratio	Cross Section Ratio
0.26 C	0.2	0.36	0.07
0.27 C	0.2	0.31	0.07
0.82 Mo + 0.25 C	0.22	0.47	0.078
1.05 Sn + 0.24 C	0.20	0.46	0.070
1.35 Sn + 0.22 C	0.20	0.51	0.070
3.0 Ta + 0.44 C	0.52	0.69	0.18
6.4 Ta + 0.56 C	0.88	0.87	0.31
0.45 W + 0.30 C	0.24	0.34	0.084
0.30 W + 0.23 N + 0.14 C	0.23	0.52	0.080
1.6 Ti + 0.21 C	0.36	0.46	0.126
3.4 Ti + 0.18 N + 0.25 C	0.54	0.97	0.19
10.4 Ti + 0.34 C	1.21	1.3	0.42
49 Ti + 0.5 Al + 1.1 C	3.7	1.9	1.29

C. Microstructure

Sections of the alloys as annealed for 7 hours at 650 C were mounted in bakelite, polished by hand to 4/0 paper, and etched with 2 per cent ammonium bifluoride and 2 per cent ammonium persulfate solution.

Except for the presence of carbides and nitrides, no second phase was detected in any of the alloys described in this report.

D. Corrosion Data

Small pieces of each alloy were corroded in a stainless steel retort with steam at 400 C. After 18 hours all the alloys were badly oxidized with the exception of the molybdenum and tin alloys. The molybdenum and tin alloys had only a very light oxide coating. Since these alloys were made of zirconium of doubtful corrosion resistance, these data cannot be taken as proof of the effect of the alloying elements on the corrosion resistance of zirconium. It does show that none of the alloying elements have the desirable effect of tin on corrosion resistance, with the possible exception of molybdenum.

E. Transformation Temperatures

As a guide to the heat treating of these alloys, and so as to obtain more information with regard to the phase diagrams of these alloys, their transformation temperatures were determined. Differential thermal analysis was used. A nickel sample was used as a reference body, and the temperature difference between this reference body and a 30-gram sample of

each zirconium alloy was measured. Chromel-Alumel thermocouples and a 0.035 micro-amp/mm galvanometer were used to record the temperature variations between the reference body and the alloy. The alloy was heated and cooled at a rate of approximately 4 C per minute. The accuracy of these determinations is ± 15 C.

The data obtained from this investigation are shown in Table IV. It is apparent that carbon and nitrogen raise the transformation temperature, and that molybdenum, tantalum, tungsten, and titanium lower the transformation temperature. Tin seems to have little or no effect upon the transformation temperature of zirconium.

F. Heat-Treating Data

Sections of the alloys as hot and cold rolled to 0.060-inch sheet were further annealed for two hours at 800 C and furnace cooled. The annealed hardness was obtained before the alloys were reheated to 800 C and quenched in water. After quenching all alloys showed a minor increase in hardness attributable to quench strains.

The same samples were then reheated to 950 C and quenched in water. All alloys showed an additional minor increase in hardness with the exception of the tin alloys. The hardnesses of the tin alloys dropped slightly below those of these alloys in their annealed condition. The quenched alloys showed no precipitation-hardening effects when aged for one-half hour and for two hours at 600 C.

The data from this investigation are shown in Table V.

TABLE IV. TRANSFORMATION TEMPERATURES OF Zr ALLOYS

Zirconium Alloys, Weight Per Cent (As Analyzed)	Transformation Range			
	On Heating		On Cooling	
	Begin, C	End, C	Begin, C	End, C
Iodide Zr*	863	899	854	827
0.26 C	885	899	882	860
0.27 C	896	935	910	866
0.82 Mo + 0.25 C	813	846	849	749
1.05 Sn + 0.24 C	882	904	893	838
1.35 Sn + 0.22 C	868	910	860	827
3.0 Ta + 0.44 C	866	882	857	816
6.4 Ta + 0.56 C	804	821	788	743
0.45 W + 0.30 C	841	868	829	788
0.30 W + 0.23 N + 0.14 C	860	891	868	821
1.6 Ti + 0.21 C	843	863	843	793
3.4 Ti + 0.18 N + 0.25 C	860	893	904	807
10.4 Ti + 0.34 C	682	693	668	604

TABLE V. HEAT-TREATING DATA

Zirconium Alloys, Weight Per Cent (As Analyzed)	Rockwell Hardness, R_A				
	Annealed At 800 C for 2 Hours	Quenched in Water From 800 C	Quenched in Water From 950 C	Aged at 600 C for One-Half Hour	Aged at 600 C For 2 Hours
0.26 C	41	48	50	51	50
0.27 C	44	49	49	50	49
0.82 Mo + 0.25 C	52	59	67	64	62
1.05 Sn + 0.24 C	54	55	51	52	53
1.35 Sn + 0.22 C	54	55	50	52	52
3.0 Ta + 0.44 C	43	50	55	55	54
6.4 Ta + 0.56 C	48	54	57	59	59
0.45 W + 0.30 C	44	46	53	57	56
0.30 W + 0.23 N + 0.14 C	62	64	63	65	64
1.6 Ti + 0.21 C	46	51	54	55	54
3.4 Ti + 0.18 N + 0.25 C	63	66	66	65	66
10.4 Ti + 0.34 C	57	59	62	61	61

CONCLUSIONS

1. Small additions of molybdenum, tantalum, tin, titanium, and nitrogen appreciably increase the high-temperature tensile strength of zirconium.

2. Zirconium alloys containing 0.82 per cent molybdenum, 1.35 per cent tin, 6.4 per cent tantalum, 0.45 per cent tungsten, and 49 per cent titanium are all solid-solution type alloys.

3. Tin and molybdenum seem to improve the corrosion resistance of low-grade iodide zirconium.

4. Molybdenum, tantalum, tungsten, and titanium lower the transformation temperature of zirconium; carbon and nitrogen raise it, and tin seems to have little effect upon the transformation temperature of zirconium.

5. The solid-solution alloys of zirconium show little promise of being improved by heat treating.

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August 24, 1951

APPENDIX

Calculation of the Neutron Cross Section of an Alloy

In the absence of data with reference to the effect of alloying elements upon the neutron absorption characteristics of a base metal, it was necessary to assume that the neutron "cross section" of an alloy is directly proportional to the atomic perecentage of the alloying elements present. For purposes of comparison, it was assumed that the neutron cross section of an alloy was equal to the sum of the products of the cross section of each element times its atomic fraction in the alloy.

Take, for example, an alloy containing 97 weight per cent zirconium and 3 weight per cent of tantalum:

Required Data:

<u>Element</u>	<u>Weight, Per Cent</u>	<u>Atomic Weight</u>	<u>Thermal Neutron Cross Section</u>
Zirconium	97	91.2	0.2 barn/atom
Tantalum	3	180.9	21.0 barns/atom

Calculate the atomic fraction of each element:

$$\text{Zr, } \frac{97}{91.2} = 1.064$$

$$\text{Ta, } \frac{3}{180.9} = 0.0166$$

$$\text{Atomic Fraction Zr} = \frac{1.064}{1.064 + 0.017} = 0.984$$

$$\text{Atomic Fraction Ta} = \frac{0.0166}{1.064 + 0.017} = 0.0153$$

Calculate the cross section contributed by each element:

$$\text{Cross Section Zr} = (0.2) (0.984) = 0.197$$

$$\text{Cross Section Ta} = (21) (0.0153) = 0.322$$

Then, the cross section of the alloy is equal to the sum of these cross sections:

$$\text{Alloy Cross Section} = 0.52 \text{ barn /atom}$$