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THE SYSTEM ZIRCONIUM-IRON-TIN

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THE SYSTEM ZIRCONIUM-IRON-TIN

ABSTRACT

A study of the solubility limits of iron and tin in alpha zirconium at temperatures below 500°C is in progress. Dilute alloys were prepared by arc-melting using the highest purity materials. Heat treatment of the alloys involves homogenization at 800°C followed by severe cold work prior to extended anneals at temperatures between 200° and 500°C in 50-degree intervals. Metallographic examination of annealed and quenched structures is the primary mode of investigation. Some magnetic susceptibility studies were also made.

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THE SYSTEM ZIRCONIUM-IRON-TIN

I. INTRODUCTION

In accordance with Contract AT(11-1)-315 entitled "A Study of the Mechanisms of Heat Treatment of Zirconium-Base Alloys," the solubility of iron and tin in alpha-zirconium below 500°C is being studied. This work is part of the supplement to the contract entitled "Phase Diagram Studies."

The approach to this investigation was based on the results of the work of the previous year in which the phase relations of the zirconium-rich corner of this system were determined between 500° and 1100°C.⁽¹⁾ Dilute alloys of the highest purity materials were made, and heat treatments between 200° and 500°C (at 50-degree intervals) are in progress. Metallographic analysis of the quenched structures is the main investigative tool. Magnetic susceptibility tests were made.

II. EXPERIMENTAL PROCEDURES

A series of 58 alloys was prepared in the form of 10-gram buttons in a nonconsumable electrode arc melting furnace. This technique utilizes multiple melting to insure homogeneity and is done in an inert atmosphere to prevent contamination. The base material was high purity, "Grade 1," iodide crystal bar (hafnium-free) supplied by the AEC. Prior to using it for melting stock it was electron bombardment melted under high vacuum by Temescal Metallurgical Corporation. The purpose of this operation was to attempt to lower the iron level and, in general, to purify the material further. The alloy constituents were added in the form of master alloys (0.5w/o Fe and 0.5w/o Sn). High purity iron was received from National Research Corporation and high purity tin from the Vulcan Detinning Company. A listing of the nominal

and analyzed compositions of the alloys appears in Table I. A plot of the analyzed compositions appears in Figure 1.

The alloys were homogenized at 800°C for 50 hours in evacuated Vycor bulbs, after cold pressing was employed to speed the approach to equilibrium. The resulting coarse-grained α or $\alpha + \beta$ structures were preserved by quenching in iced brine. The ingots were then severely cold worked by both pressing and rolling to an approximate thickness of 3/16 in. Specimens of about 1/4 in. square were cut from the resulting material. Great care was taken to keep the alloys clean by frequent pickling treatments in 20% HNO₃-5% HF solution followed by water and acetone rinses.

Equilibration anneals were set between 200° and 500°C inclusive at 50-degree intervals. Since transformations at such low temperatures are so sluggish, the greater the length of time at temperature the more likely equilibrium will be reached. Therefore, the tentative schedule of 1500 to 2000 hours (or more if time permits) was decided upon. Duplicate samples annealed at 400°, 450° and 500°C for 429 hours were examined metallographically after quenching in iced brine and compared with structures quenched from 800°C to determine if there were any observable transformations.

Since ZrFe₂ was found to be ferromagnetic, it was felt that magnetic susceptibility measurements could prove to be an accurate method for determining the presence or absence of this compound in a non-ferromagnetic matrix. The susceptibility apparatus used was of the Curie⁽²⁾ type and incorporated an analytic balance to measure the magnetic force on samples suspended in the field of an electromagnet. The system was calibrated using a standard sample of palladium. Alloys used in determining the feasibility of this technique were from last year's program.

III. RESULTS AND DISCUSSION

A. Metallography

Three ingots of zirconium were prepared by electron bombardment melting. The one with the lowest hardness (VPH 69) and the cleanest microstructure was used in this work. Spectrochemical analysis indicated that the level of iron remained at the same order of magnitude of the original material (27 ppm). The process had a remarkable effect on the microstructure as is seen when comparing the structure of arc-melted iodide crystal bar (Figure 2) and that of electron bombardment melted stock (Figure 3). The majority of the precipitate in the former appears to be hydride. Arc melting the latter material brings about a somewhat dirty structure once again (Figure 4). Chemical analyses of the zirconium in the various conditions are found in Table II, indicating that all the melting results in some degree of impurity pickup. Aside from the increase in hydrogen in the arc-melted iodide crystal bar, which would explain the hydride seen in Figure 2, the pickup is quite small.

Hydrogen would be the only impurity that would be expected to show up in the microstructure. This points to the possibility that some of the precipitate is either $ZrFe_2$ or Zr_4Sn . The precipitate is also evident in structures quenched from 800°C where only α or $\alpha + \beta$ would be expected in pure zirconium or the dilute alloys used in this study. This is seen in Figure 5 of alloy No. 341 (0.05w/o Fe) annealed for 50 hours at 800°C and quenched in iced brine. At this point it is not known whether the precipitate is in equilibrium at this temperature or comes out during quenching. An attempt to study some critical alloys in the hot stage microscope will be made and should shed light on this question.

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Short-time anneals (429 hours) at 400°, 450° and 500°C were insufficient to bring the alloys to equilibrium as is evidenced by the presence of β in the 0.05w/o Fe alloy quenched from 450°C in Figure 6. Recrystallization has taken place, but the varied grain size indicates that this process has not gone to completion either. Thus, interpretation of microstructures will be made of specimens which have been annealed for extended periods of time.

B. Magnetic Susceptibility

The susceptibility of paramagnetic and diamagnetic samples is independent of the magnetic field strength. However, when small amounts of ferromagnetic components are imbedded in a non-ferromagnetic matrix, the apparent susceptibility of the combination may be shown to obey a relationship of the form:⁽²⁾

$$k_H = k_\infty + CM_S/H,$$

where k_H is the apparent susceptibility at field strength H , k_∞ is the true susceptibility of the matrix, C is the concentration of the ferromagnetic component, and M_S is its saturation magnetic moment. According to this equation, a plot of measured susceptibility versus $1/H$ should yield a straight line. The magnitude of the slope (CM_S) is a measure of the amount of ferromagnetic material present. Furthermore, the intercept, k_∞ , is the true susceptibility of the matrix.

The results of these tests are summarized in Table III and in Figure 7. The susceptibility of pure zirconium is known to be -0.45×10^{-6} emu/gram. This value (negative) is indicative of diamagnetism while the results of this study show paramagnetic behavior (e.g., of the order of 1.5×10^{-6} emu/gram). This would be expected to be due to the presence of a paramagnetic impurity such as oxygen. It is seen that within the sensitivity of this

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apparatus the technique is effective in determining the presence of $ZrFe_2$ when this compound is present in substantial amounts. The microstructure of the two 3-phase alloys (lw/o Fe-0.5w/o Sn and lw/o Fe-lw/o Sn) showed smaller amounts of $ZrFe_2$ than found in the lw/o Fe alloy. Thus, this technique is not considered sensitive enough for further work with the extremely dilute alloys of this investigation since even smaller quantities of $ZrFe_2$ would be expected in these alloys.

IV. FUTURE WORK

The specimens, which are undergoing extended heat treatments, will be examined metallographically.

V. CONTRIBUTING PERSONNEL AND LOGBOOKS

Data relating to the work reported herein are recorded in ARF Logbook C-5826.

The following personnel have contributed to the work:

J. J. Brophy	Magnetic Susceptibility Data
W. A. Buknas	Heat Treatment
D. W. Levinson	Supervisor
L. C. Malevitis	Arc Melting
R. E. Steiner	Arc Melting
B. J. Stang	Metallography
L. E. Tanner	Project Leader
M. Wright	Project Technician

Respectfully submitted,

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REFERENCES

1. Tanner, L. E. and D. W. Levinson, "The System Zirconium-Iron-Tin," Summary Report ARF-2068-4, Contract No. AT(11-1)-315, Aug. 12, 1957.
2. Bates, L. F., Modern Magnetism (Cambridge University Press, 1951) p. 122.

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TABLE I
COMPOSITIONS OF Zr-Fe-Sn ALLOYS

Alloy No.	Iron (w/o)		Tin (w/o)	
	Nominal	Analyzed	Nominal	Analyzed
300	0.500	0.450		
301			0.500	0.520
302	0.005	0.017		
303	0.010	0.012		
304	0.015	0.025		
305	0.020	0.028		
306			0.050	0.060
307			0.100	0.110
308			0.150	0.150
309			0.200	0.190
310			0.300	0.270
311			0.400	0.360
312			0.500	0.450
313			0.600	0.510
314			0.700	0.610
315			0.800	0.760
316	0.002	0.027	0.020	0.050
317	0.002	0.006	0.050	0.040
318	0.002	0.008	0.070	0.070
319	0.002	0.006	0.170	0.160
320	0.004	0.009	0.090	0.090
321	0.004	0.005	0.190	0.170
322	0.005	0.011	0.020	0.040
323	0.006	0.012	0.050	0.100
324	0.006	0.007	0.110	0.100
325	0.006	0.006	0.210	0.190
326	0.008	0.010	0.180	0.170
327	0.008	0.012	0.280	0.270
328	0.009	0.009	0.020	0.030
329	0.010		0.050	
330	0.010	0.015	0.250	0.245
331	0.010	0.017	0.400	0.379
332	0.011	0.013	0.110	0.107
333	0.012	0.015	0.270	0.251
334	0.012	0.027	0.420	0.400
335	0.013	0.014	0.130	0.170
336	0.014	0.019	0.050	0.054
337	0.014	0.015	0.440	0.420
338	0.015	0.018	0.150	0.130
339	0.016	0.019	0.460	0.433
340	0.017	0.017	0.170	0.150

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TABLE I (continued)

Alloy No.	Iron (w/o)		Tin (w/o)	
	Nominal	Analyzed	Nominal	Analyzed
341	0.018	0.047	0.050	0.047
342	0.018	0.070	0.480	0.450
343	0.019	0.023	0.190	0.180
344	0.020	0.028	0.500	0.360
345	0.021	0.023	0.210	0.190
346	0.022	0.025	0.050	0.046
347	0.023	0.026	0.230	0.210
348	0.030	0.030		
349	0.040	0.050		
350	0.050	0.051		
351	0.060	0.066		
352	0.070	0.038		
353	0.080	0.070		
354	0.090	0.072		
355	0.100	0.090		
356	0.300	0.300		
357	0.500	0.460		
358	0.700	0.630		
359	1.000	0.980		

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TABLE II
ANALYSES FOR NITROGEN, OXYGEN
AND HYDROGEN IN PURE ZIRCONIUM

Material	Nitrogen (w/o)	Oxygen (w/o)	Hydrogen (ppm)
Iodide crystal bar, as received	nil	0.0037	nil
Iodide crystal bar, arc melted	0.010	0.0092	30
Electron bombardment melted, as received	0.0009	0.019	4
Electron bombardment melted, arc melted	0.0024	0.020	10

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TABLE III
SUSCEPTIBILITY MEASUREMENTS OF ZIRCONIUM-BASE ALLOYS

<u>Composition</u>		<u>Heat Treatment</u>	<u>Structure</u>	<u>Results</u>
<u>w/o Fe</u>	<u>w/o Sn</u>			
0	0	600 hr-600°C-WQ	α	paramagnetic*
0	24.5	150 hr-700°C-WQ	nearly 100% $\text{Zr}_{14}\text{Sn}(\theta) + \alpha$	paramagnetic
1	0	300 hr-750°C-WQ	$\alpha + \text{ZrFe}_2$	ferromagnetic
5	0	600 hr-600°C-WQ	$\alpha + \text{ZrFe}_2$	ferromagnetic
1	0.5	744 hr-600°C-WQ	$\alpha + \theta + \text{ZrFe}_2$	paramagnetic
1	1	744 hr-600°C-WQ	$\alpha + \theta + \text{ZrFe}_2$	paramagnetic
1	9	744 hr-600°C-WQ	$\alpha + \theta$	paramagnetic
2.5	15	508 hr-700°C-WQ	$\alpha + \theta$	paramagnetic

* All paramagnetic samples have a susceptibility of the order of 1.5×10^{-6} emu/gram.

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FIG. 1 - ANALYZED COMPOSITIONS OF ZIRCONIUM-BASE ALLOYS WITH IRON AND TIN

Neg. No. 16140

X 250

Fig. 2

Arc melted iodide zirconium crystal bar.

Neg. No. 16138

X 250

Fig. 3

Electron bombardment melted iodide zirconium crystal bar.

Neg. No. 16143

X 250

Fig. 4

Arc melted, electron bombardment melted iodide zirconium crystal bar.

Etchant: 20% HF, 20% HNO₃ in glycerine.

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Neg. No. 16237

X 250

Fig. 5

A 0.05w/o Fe alloy (No. 341) annealed at 800°C for 50 hours and quenched in iced brine. Large α grains with β at the grain boundaries.

Neg. No. 16238

X 250

Fig. 6

A 0.05w/o Fe alloy (No. 341) annealed at 450°C for 429 hours and quenched in iced brine. Recrystallized α plus unresorbed β .

Etchant: 20% HF, 20% HNO₃ in glycerine.

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FIG. 7 - SUSCEPTIBILITY OF ZIRCONIUM-BASE ALLOYS
AS A FUNCTION OF RECIPROCAL MAGNETIC FIELD