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ANNEALING OF IRRADIATED BORON CONTAINING ALLOYS AND DISPERSIONS

by

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ANNEALING OF IRRADIATED BORON CONTAINING ALLOYS AND DISPERSIONS

I. INTRODUCTION

The interpretation of the dimensional instability of U-Zr alloy containing small amounts of boron has raised the question of whether the observed low temperature swelling can be related to the temperature-swelling characteristics of either the U-Zr alloy or Zr-B alloys by themselves. To obtain such information on the Zr-B system to compare with the more detailed study of the alloy early results of which were reported in KAPL-1562 pieces of previously irradiated Zr-B alloys and dispersions were annealed in vacuum at temperatures between 350°C and 750°C.

Explanation

A. Materials - The alloys and dispersions were unclad, rectangular cross section, bend test specimens. The fabrication history has been described by A.P. Beard.⁽¹⁾ The material was irradiated in helium-cooled assemblies in the MTR at a thermal flux level of 2×10^{-14} nv or higher. The material is identified as follows:

Irradiation No.

Material

28-10-2	.21 wt % B ¹⁰ alloyed in Zr-2	50% of B ¹⁰ or 1.1 at.% total core atoms
28-1	.78 wt % B ¹⁰ alloyed in Zr	40% of B ¹⁰ or 2.6 at.% total core atoms
28-12-2	.35 wt % B ¹⁰ dispersed in Zr	37% of B ¹⁰ or 1.0 at.% total core atoms
28-15-2	1.2 wt % B ¹⁰ dispersed in Zr	99% of B ¹⁰ * or 2.0 at.% total core atoms

*Of questionable accuracy

B. Experimental Procedure

A small quartz tube furnace was installed in the beta cave annealing cell. The furnace closure was made with an "O" ring and an aluminum face plate. The furnace was evacuated to a furnace pressure of 1-2 microns by means of a high vacuum system located outside the cell and connected to the furnace by 3/8 I.D. copper tubing. The forepump was vented into the cell.

Before annealing, density, dimensional and electrical resistance measurements were made on the sample. These measurements were repeated after each annealing period. A constant annealing time of 24 hours was used. The temperature was raised 50 degrees Centigrade at each successive annealing period until the experiment was terminated at 750°C.

Results and Discussion

The resulting volume changes are shown in figure 1. The dispersions are observed to undergo the least dimensional changes. This result is tempered by the fact that the amount of helium (if any) escaping during the annealing was not measured and that the dispersions would be more likely to lose gas at low temperatures than would the alloys. Gas that has escaped could not cause swelling. The amount of gas remaining in the samples is being determined to see if a significant amount has escaped. The alloy samples were found to be extremely brittle both before and after annealing. The dashed line on graph in figure 1 is the swelling curve vs. temperature for 7 wt % U-Zr alloy in 24 hours at approximately 1 at.% burnup as obtained from steady state measurements using a different sample at each temperature;* it is noted that accelerated swelling occurred at a lower temperature in Zr-U alloy than in Zr-B alloy. Because of the strong possibility that nucleation and growth phenomena are responsible for differences in the swelling at various temperatures (presumably less swelling results when nucleation occurs at low temperatures because the small bubbles are held by surface tension), the Zr-B material may not have begun to swell appreciably at as low a temperature as the U-Zr. Another explanation is that there is no metallurgical transformation in the Zr-B alloy over the temperatures studied.

The change in electrical resistivity as a function of annealing temperatures is shown in figure 2. Two occurrences are worthy of comment here. (1) The dispersions recovered the least at the lower annealing temperatures and gained the most at higher temperatures. (2) Sample 28-12-2 which did not swell during annealing, did undergo nearly the same resistivity changes as the dispersion that did swell. This indicates that the electrical resistivity measurements may not look at the same effects as do the density changes. The observed resistivities may be the difference between two effects - an initial annealing of radiation damage to the zirconium followed by increases in resistance related to an increase in defects (vacancies) around the damaged regions as Cottrell² has postulated, or simply the diffusion of lithium away from the boron and into the undamaged region.

The change in thermal conductivity was computed from¹ the electrical resistivity by means of the empirical Wiedemann-Franz ratio for zirconium alloys as reported by Bing³. The results are shown in Table 1. The as-irradiated values are in agreement with the earlier measurements reported in KAPL Memo WVJ-1. The dispersions, although having a higher conductivity than the alloys, have undergone as high a percentage change in thermal conductivity during irradiation as have the alloys. If it is valid to make the simple assumption that in a dispersion of a non-electrical conducting material in a conducting matrix the increase in resistance is directly proportional at constant total volume to the volume fraction of the dispersed material, then a calculation of the fraction of the matrix that would be damaged by recoils during irradiation should approximate the observed resistivity change. Since the volume fraction of boron in a 1.2 wt % dispersion is about .033 and the particle size is 100-200 micron, a computation based upon² a close packed sphere model⁴ yields only a 0.5% damaged volume. Since the observed changes are much greater than this, some other effects must predominate. There are two possibilities that can explain the observed effects. The

*Unpublished KAPL data. Work in progress.

diffusion of the irradiation produced lithium into the matrix is one possibility. The diffusion coefficient of lithium in zirconium is not known but a D of only 10^{-11} at irradiation temperature would be sufficient for lithium to diffuse throughout the specimen. The second possibility is that since the boron and zirconium powders used as starting materials were not of as high a quality as is now available and the fabrication technique was new that considerable fragmentation and clumping occurred during fabrication. This non-uniform distribution could result in considerable localized damage to a large cross sectional area of the sample. Metallographic examination, not yet completed, should be of help in the interpretation of these results. In addition to the optical examination, electron microscopy and a chemical dissolution for remaining gas is planned for these samples.

Proposed Future Work

A second series of experiments designed to tie in better with the U-Zr annealing studies is proposed. It will be conducted using four additional samples of the same material. The test conditions are as follows:

1. Annealing temperature - 5400°
2. Annealing time - 4 periods of 24, 36, 90 and 250 hours for a total of 400 hours.
3. Annealed in Vacuum

Measurements

1. Density	}	Both before and
after each annealing period
2. Electrical Resistivity		
3. Physical Dimension		
4. He Release		
-
- (a) Mass spectrometric analysis of total amount of gas given off by each sample, collected at the termination of each annealing period.
 - (b) Intermediate mass spectrographic sampling of the gas during each annealing period.
 - (c) Rate of gas release by pressure change in the collection system.
 5. Metallographic examination after the final annealing period.
 6. Chemical dissolution to determine amount of gas retained by samples after final annealing period.
 7. Micro hardness test before first anneal period and after the last anneal period.

TABLE I

PERCENTAGE DECREASE IN THERMAL CONDUCTIVITY K (watts/ $^{\circ}$ C/cm)
RELATIVE TO PRE-IRRADIATION VALUES

	28-15-2a	28-12-2a	28-10-2	28-1-1aS-C16
B.U.	1 %	1 %	1 %	2.6 %
As irradiated	18.1	14.0	12.0	31.6
After 24 hrs. @ 350 $^{\circ}$ C	15.7	10.8	6.8	(a)
After 24 hrs. @ 400 $^{\circ}$ C	15.1	11.5	4.5	
450 $^{\circ}$ C	15.1	12.1	3.8	
500 $^{\circ}$ C	19.3	12.7	3.8	
550 $^{\circ}$ C	16.3	13.4	3.8	
600 $^{\circ}$ C	17.5	15.9	5.3	
650 $^{\circ}$ C	19.9	19.1	7.5	
700 $^{\circ}$ C	22.9	21.7	12.8	
After 24 hrs. @ 750 $^{\circ}$ C	24.7	25.5	—	

(A) Sample broke and became too short for further measurement

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