BUBBLE FORMATION IN ZR ALLOYS UNDER HEAVY ION IMPLANTATION

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ABSTRACT

We report here the results of a study conducted to examine the effect of Kr ion irradiation on bubble formation in Zr alloys. We used the HVEM/Tandem facility at Argonne National Laboratory to irradiate several Zr alloys, including Zircaloy-2 and Zircaloy-4, at temperatures from 300 to 800 C and to doses up to 2 x 10^{16}ion.cm^{-2}. Both in-situ irradiation of thin foils as well as irradiation of bulk samples with an ion implanter were used in this study. For the thin foil irradiations, a distribution of small bubbles in the range of 30-100 Å was found, at all temperatures with the exception of the Cr-rich Valloy where bubbles of 130 Å were found. The irradiation of bulk samples at high temperature (700-800 C) produced large faceted bubbles (up to 300 Å) after irradiation to 2 x 10^{16} ion.cm^{-2}. The results are examined in the context of existing models for bubble formation and growth in other metals.

INTRODUCTION

Zirconium alloys have been used for nuclear reactor fuel cladding for the last 40 years because of their combination of low neutron absorption, excellent resistance to high temperature corrosion, and good mechanical properties [1]. Their response to radiation damage has been extensively studied [1,2]. In particular they undergo radiation creep and growth but in contrast to steels do not exhibit void swelling. The absence of voids in neutron irradiated zirconium alloys has been explained by the fact that *both* vacancy and interstitial loops form under irradiation, that is, the void embryos collapse to loops which are stable [3].

Small voids have been occasionally reported in zirconium alloys, such as Zircaloys [4], specially after implantation with ions [5,6]. This suggests that bubble formation could be induced in zirconium alloys by ion implantation under suitable conditions. We have in this work conducted a systematic study of the conditions of bubble formation in zirconium alloys under Kr ion irradiation. The objective was to determine the boundaries of the different regimes of bubble behavior, specially the regions of gas and bubble mobility that enable the formation of larger bubbles by coalescence. A second goal was to derive mechanistic understanding of the process of bubble formation and growth in zirconium alloys under irradiation.

EXPERIMENTAL METHODS

Five different materials were tested: four commercial alloys, (Zircaloy-2, Zircaloy-4, Valloy, NSF) and nominally pure zirconium. The commercial alloys were furnished by GE, and the Zr (99.8%) was obtained from Goodfellow. The composition of these alloys (in wt. %) is given in table 1.

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Table 1 - Chemical Composition (wt %) of the Studied Materials

Alloy	Sn	Fe	Cr	Ni	Nb
Zircaloy 4	1.5	0.21	0.1	*	*
Zircaloy 2	1.6	0.15	0.1	0.05	*
NSF	1.0	0.2	*	0.05	0.6
Valloy	*	0.1	1.1	*	*
Zr-NP	impurities less than 0.2 wt%				

* trace amounts

Samples were mechanically polished and ground to 0.1 mm thick disks. Thin foils samples from all materials were prepared from these disks by electropolishing with a 100 ml of butyl cellosolve in 500 ml of methanol [with 5.3 g of LiCl and 11.16 g of $Mg(ClO_4)_2$] at -30 C [7]. Bulk samples of Zircaloy-4 were prepared, by electropolishing one face before irradiation and the second face after irradiation.

An implantation energy of 100 keV for the Kr^+ beam was selected based on the TRIM code [8], which gave an implantation range of 45 nm The implantation energy was chosen so that the ion range was about half the foil thickness to maximize the retention of krypton in the samples. Implantation was performed at the HVEM/Tandem Facility [9] at the Center for Electron Microscopy at Argonne National Laboratory using either an ion implanter for thin and bulk samples, or a High Voltage Electron Microscope for thin samples. The level of damage calculated by TRIM at the half maximum of the Bragg peak was 1 dpa per 4.4 x 10^{14} ion.cm^{-2}, using E_d=25 eV. Vacuum inside the HVEM was better than 2 x 10^{-7}. torr.

The post-irradiation examinations were performed in a JEOL JEM-100CX at Argonne National Laboratory, and in a Philips 420T at the Materials Characterization Laboratory at Pennsylvania State University, operating at voltages of 100 keV and 120 keV, respectively. The irradiation temperature and dose ranges were from 300 C to 800 C and from 1 x 10^{16} to 2 x 10^{16} ions.cm^{-2}, respectively

RESULTS

Examination of the irradiated samples revealed that bubbles are formed in zirconium alloys by irradiation with 100 keV Kr ions. A wide variety of bubble size distributions was found, by changing the irradiation temperature and irradiation conditions (bulk samples versus thin foil). In general the thin foil samples exhibited small bubbles in the range of 50 Å, irrespective of irradiation temperature. The one exception to that behavior were the Valloy samples where slightly larger bubbles (up to 130 Å) were seen. In contrast, bulk samples at high temperature tended to form large faceted bubbles.

Figure 1 shows the electron micrographs of thin foil irradiation of Zircaloy 4 (a) and Valloy (b), after irradiation to 2 x 10^{16} ion.cm^{-2} at 700 C. The Zircaloy-4 picture is typical of the other alloys and temperatures from 300 to 700 C: only small bubbles, homogeneously distributed through the lattice are observed. Valloy by contrast, exhibited small agglomerations of larger bubbles (arrowed), in addition to the background of small bubbles. It is not clear at this point whether the

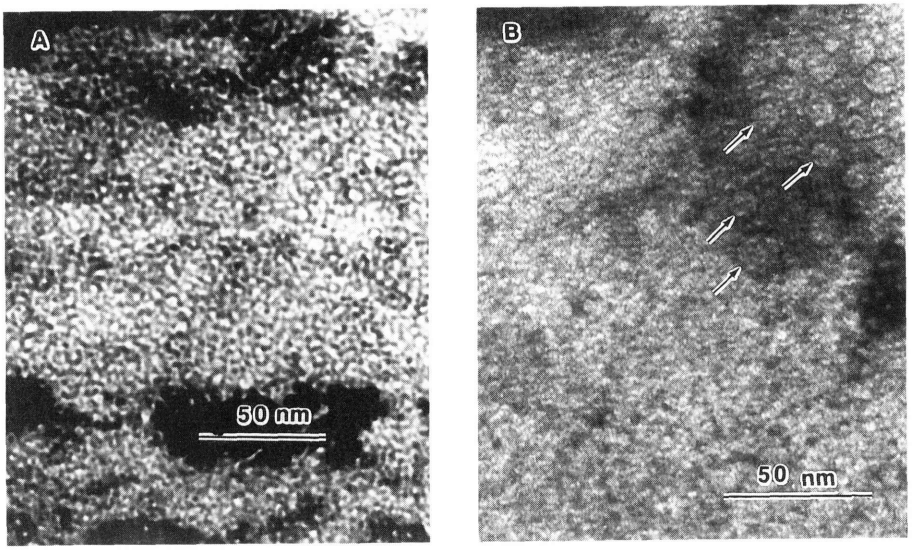

Figure 1: Bright field micrographs of thin foils of (a) Zircaloy-2 and (b) Valloy after irradiation with 100 keV Kr at 700 C to 2 x 10^{16} ion.cm^{-2}.

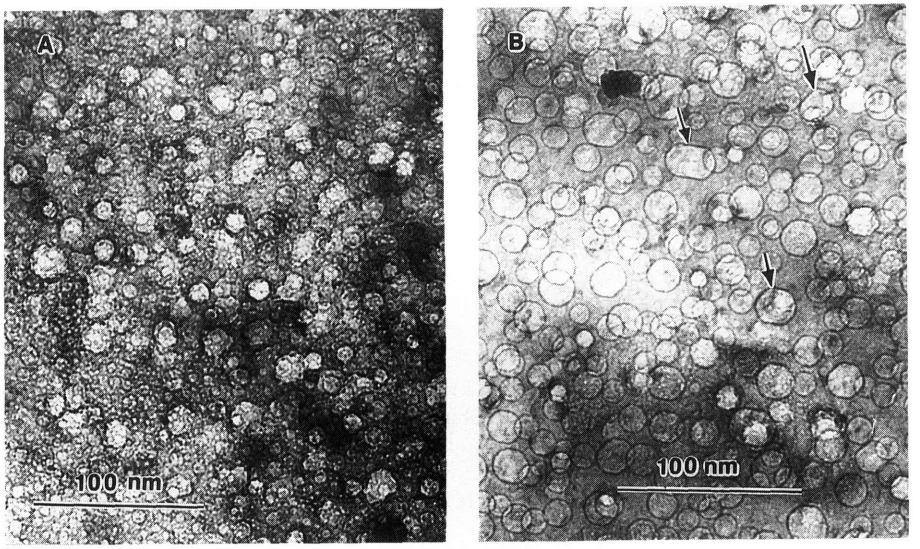

Figure 2 : Bulk samples of Zircaloy-4 irradiated with 100 keV Kr ions at (a) 700 C to 1 x 10^{16} ion.cm^{-2} and (b) 800 C to 2 x 10^{16} ion.cm^{-2}..

agglomerations are due to thickness variations in the TEM foil, or whether they are associated with second phase precipitates.

Figure 2 shows the distribution of bubbles after bulk irradiation to 1 x 10^{16} ion.cm^{-2} at 700 C (a) and 2 x 10^{16} ion.cm^{-2} at 800 C (b). Large faceted bubbles are seen, with sizes up to 300 Å. Some bubble coalescence was observed (arrowed in the pictures). The bubbles were homogeneously distributed over the whole sample; no preferential agglomeration was detected at the grain boundaries. The size of the bubbles increases from the thin foil irradiation to the bulk irradiation and increases as the irradiation temperature increases from 700 to 800 C. It should be noted that the small bubble distribution present in the low temperature samples is still present in the high temperature ones, in addition to the large bubbles.

The distribution of bubbles is shown in quantitative form in figures 3 and 4. Figure 3 shows the variation of bubble size distribution (in bubbles.m^{-2}) in Zircaloy-4 for both thin foil and bulk irradiations as a function of temperature. All the samples showed a large density of small bubbles, but there is a marked difference between the bulk and thin foil irradiations, which is also evident by comparing figures 1 and 2. This suggests that the presence of the thin foil surfaces suppressed bubble growth, possibly by serving as a sink for vacancies, bubbles or gas atoms. We can also note the effect of dose by comparing the curves for 800 C bulk irradiations at 1 and 2 x 10^{16} ion.cm^{-2}. There is an increase in bubble size and a broadening of the size distribution as the dose is increased.

Figure 4 shows the effects of alloy composition for thin foils for a range of temperatures in Valloy, nominal purity Zr, NSF and Zircaloy-2. The behavior for all the alloys was very similar: a high density of small bubbles was formed in all cases. It can also be seen that there is a slight difference between the bubble size distribution in Valloy and that of other alloys: there is at 300, 500 and 700 C a tail in the Valloy distribution extending to 130 Å. Work is ongoing to understand the mechanistic reasons for this difference.

Samples were examined at 1 and 2 x 10^{16} ion.cm^{-2} for bulk irradiation at 800 C and thin foil irradiation at 500 C. Bubble size increased by approximately 30-40 % in each of these cases, and the bubble size distribution broadened. Attempts to follow the growth kinetics of individual bubbles were unsuccessful because of poor imaging conditions in the microscope. Some samples previously irradiated on bulk were later re-irradiated in the microscope with both electrons and ions. As far as could be ascertained, there was no obvious change in bubble size after re-irradiation [12]

Concerning the mechanisms of bubble formation and growth in Zr alloys under Kr ion irradiation, the work is still in progress. The fact that large bubbles grow during high temperature bulk irradiation and that bubble coalescence is observed indicates that large bubbles are mobile at higher temperatures. If they are mobile at those temperatures then their absence in the 700 C thin foil irradiation can be ascribed to the loss of bubbles to the thin foil surface.

It is possible that the bubbles start out containing solid Kr in the initial stages of their formation. They then become mobile by melting at an intermediate stage in their growth. At that point they can grow by coalescence with other bubbles until their increased size renders them immobile [10]. Such a mechanism has been observed in Kr ion irradiation of Ni [11]. In the thin foil case, they are

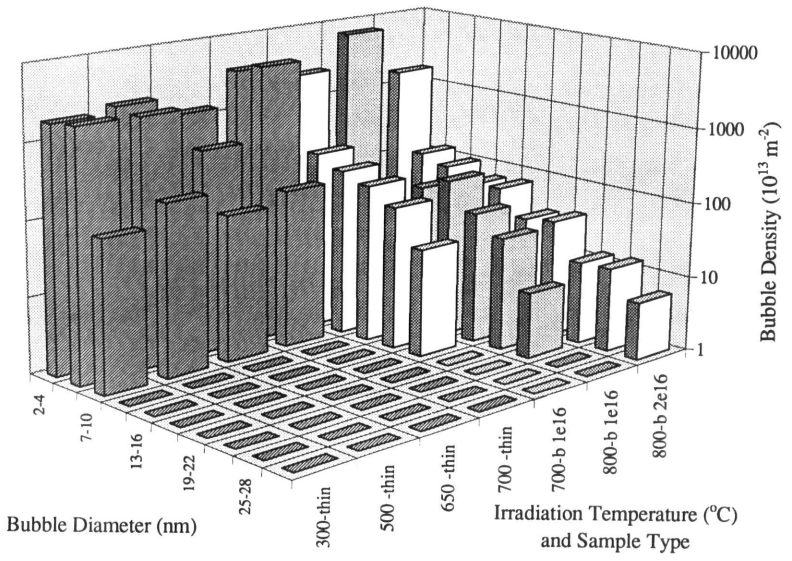

Figure 3: Bubble size distribution for Zircaloy-4 after irradiation at various temperatures with 100 keV Kr ions under bulk and thin foil conditions to 1 or 2 x 10^{16} ion.cm^{-2}.

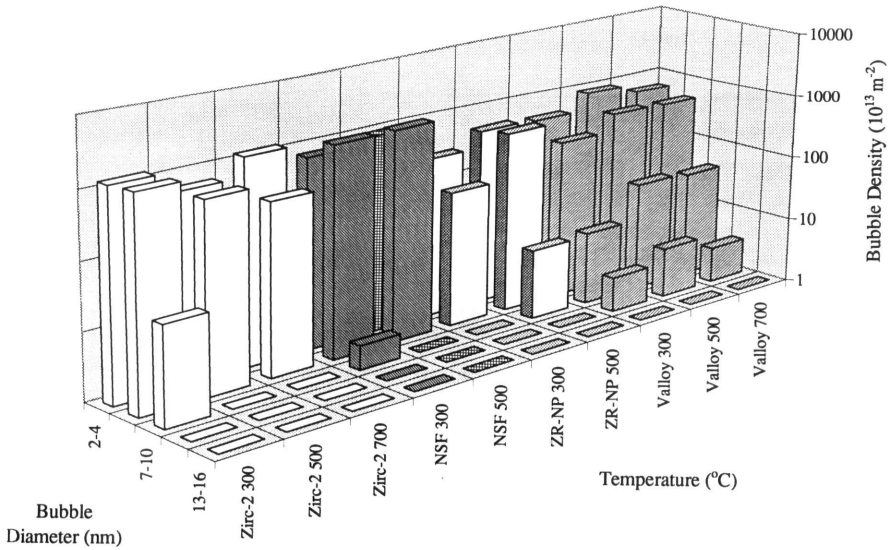

Figure 4: Bubble size distribution for thin foil irradiation of Zircaloy-2, NSF, Zr-NP and Valloy at various temperatures after 100 keV Kr ion irradiation to 2 x 10^{16} ion cm^{-2}.

lost to the thin foil surface while they are still mobile, which effectively chops off the large bubbles from the size distribution.

CONCLUSIONS

1. Samples of zirconium alloys were irradiated with 100 keV Kr ions to fluences of up to 4 x 10^{16} ion.cm^{-2}. The presence of the Kr gas allowed the formation of bubbles of up to 300 Å diameter, at the higher temperatures.

2. For the bulk samples, bubble size increased with irradiation temperature and ion dose. For the thin samples, one alloy (Valloy) showed larger bubbles (130 Å) than the others (bubbles < 100 Å)

3. There was a marked difference in behavior between irradiations conducted in pre-thinned foils and in bulk samples. The presence of the foil surfaces inhibited bubble formation and growth, possibly by acting as a sink for defects and for gas atoms.

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