X-Ray Diffraction Studies of Pile-Irradiated Hafnium Hydrides[1]

We are concerned, in this paper, with the structural stability of metal hydrides and deuterides in general and of hafnium metal in particular, after they are exposed to pile radiations, consisting of thermal neutrons, epi-cadmium neutrons and gamma rays. Would a metal hydride in which the metal atoms occupy positions that are different from those in the pure metal, due to bonding with hydrogen or deuterium atoms, maintain its crystal structure or undergo a change when it is irradiated in the pile? Approximately what dose of pile flux can such a structure stand?

Experimental Procedure

The samples selected for irradiation were $HfD_{1.63}$, HfH_2, and $HfH_{1.8}$. The deuteride, (*1*), $HfD_{1.63}$, is cubic with a CaF_2-type structure in which about 18% of the deuterium sites are vacant; the hydride (*2*), HfH_2, is tetragonal with axial ratio less than one, and the hydride (*2*), $HfH_{1.8}$, contains both the cubic and the tetragonal phases. Before irradiating, an x-ray diffraction pattern, interplanar spacings, crystal structure, dimensions of the unit cell, degree of crystallinity, etc., for each sample were determined. Then, a specimen of each sample was wrapped in a 5-mil thick aluminum foil, placed in an aluminum can, and irradiated for 635 hours in the heavy water reactor. The thermal neutron flux was 4.5×10^{12} neutrons per cm^2 per sec; epicadmium neutron flux, 3×10^{11} neutrons per cm^2 per sec; and gamma-ray flux, 1600 roentgens per sec. The surface area of each specimen was 0.5 cm^2. The specimens received irradiation of 5×10^{18} neutrons of thermal flux, 3.4×10^{17} neutrons of epi-cadmium flux and 0.4×10^{10} roentgens of gamma-ray flux. The average temperature of the specimens during irradiation was 45°C.

The specimens were radioactive when they were taken out of the pile, the activity level being too high to make x-ray diffraction patterns for comparison with those that were made before irradiation. The irradiated specimens, therefore, were stored and kept at room temperature to "cool off." Occasional radiation checks were made to determine the safe level of activity, and after about a year it was possible to make their diffraction patterns. Since the two sets of patterns, taken before and after irradiation, were to be compared, every effort was made to duplicate the conditions for preparation of the patterns.

Discussion of Results

The cubic phase of hafnium-deuterium or hafnium-hydrogen systems exists in a very narrow range of compositions. The reason for irradiating the deuteride $HfD_{1.63}$, was to see if, due to irradiation, this structure would revert to one of lower composition. As shown in Fig. 1, the diffraction patterns taken before and after irradiation are identical. There was no observable change in the crystal structure of the deuteride.

Since the hydride HfH_2 contains a stoichiometric amount of hydrogen, and all hydrogen atom sites in the lattice of the hydride are filled, the material will be relatively more sensitive to a change in its structure, if irradiation could affect either the amount of hydrogen or the positions of hydrogen atoms, or both, in the lattice. As seen in Fig. 2, the diffraction lines of the irradiated specimen are broader than those of the unirradiated specimen, indicating an effect of irradiation, or of other causes such as variation in the specimen size, eccentricity of the position of the specimen in the camera, but there was no change in the crystal structure of the material.

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

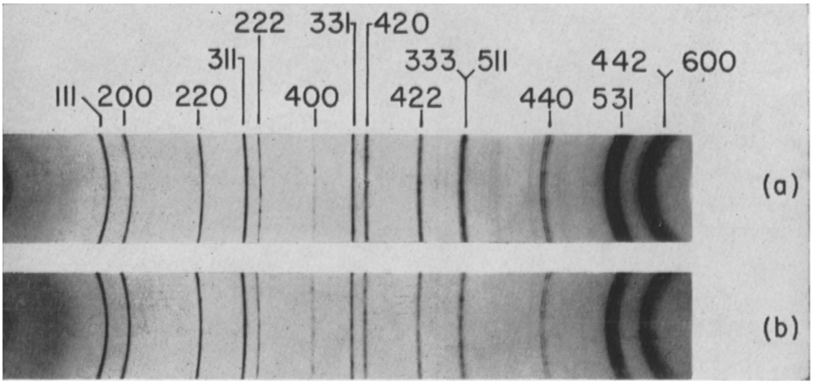

FIG. 1. X-ray diffraction patterns of $HfD_{1.63}$; (a) before and (b) after irradiation; filtered CuKα radiation; camera diameter 114.6 mm.

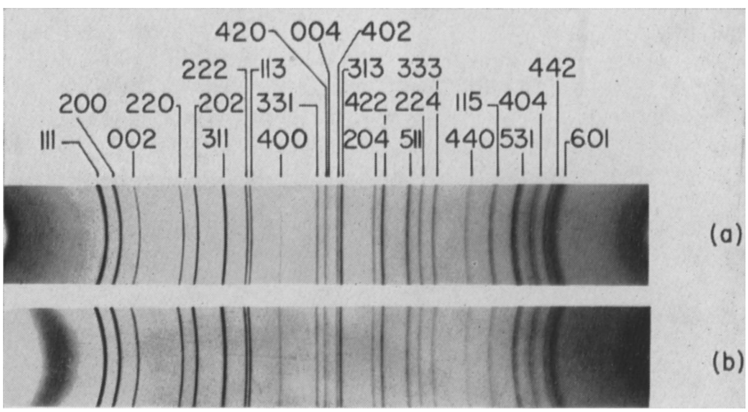

FIG. 2. X-ray diffraction patterns of HfH_2 ; (a) before and (b) after irradiation; filtered CuKα radiation; camera diameter 114.6 mm.

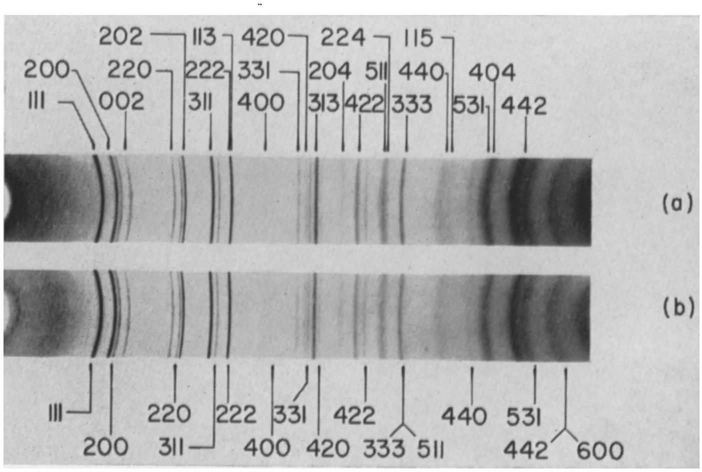

FIG. 3. X-ray diffraction patterns of $HfH_{1.8}$; (a) before and (b) after irradiation; filtered CuKα radiation; camera diameter 114.6 mm.

The hydride $HfH_{1.8}$ also exists in a narrow range of compositions, and, in addition, the fact that it contains both the cubic and the tetragonal phases of the hafnium-hydrogen system, makes it a suitable sample for irradiation. A very small change in the composition of the sample, if it can be affected by irradiation, may change the two-phase diffraction pattern to one of a single phase. As seen in Fig. 3, however, no such change was observed.

Conclusions

It is apparent that when hafnium hydrides and deuterides were exposed to heterogeneous pile radiation flux for a period of a month at an average temperature of 45°C and given a total amount of each radiation, as mentioned above, their x-ray diffraction patterns, taken after a "cooling-off" period of a year, showed no change in their crystalline structures, nor was there any visible change in the color of the specimens at the time the diffraction patterns were made. Since the stability of a crystalline structure depends upon the bonds among the atoms and the molecules that make up a structure, it would seem that the bonds between metal-metal, metal-hydrogen, and hydrogen-hydrogen atoms in the hydrides studied here were either never impaired or they reestablished themselves during or after the irradiation. It must be emphasized, however, that the stability of the crystalline structure is viewed in terms of the type and the quantity of radiation employed in this investigation. Longer exposures or more intense radiation may cause damage to the same materials and result in changes in their crystalline structures.

In view of the results obtained here it would be of interest to know if the hydrides of titanium, yttrium, and zirconium metals, that are of similar structures as those of hafnium metal, would show the same stability to pile radiations.

REFERENCES

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Received October 7, 1957
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